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MANGANESE; ITS OCCURRENCE, MILLING, AND METALLURGY

PART I.

CHAPTER 1. PHYSICAL PROPERTIES AND PREPARATION OF METALLIC MANGANESE

CHAPTER 2. MANGANESE IN NONFERROUS ALLOYS

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CHAPTER 4. OCCURRENCE AND ORE-DRESSING POSSIBILITIES OF ORES OF MANGANESE IN THE UNITED STATES

BY

R. S. DEAN, FRED D. DEVANEY AND WILL H. COGHILL

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MANGANESE: ITS OCCURRENCE, MILLING, AND METALLURGY[1]

Part I

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INTRODUCTION

This circular presents part I of a summary of the occurrence, milling, and metallurgy of manganese in the United States. An attempt has been made to assemble the data on manganese and its metallurgically important compounds which have been obtained in several years of research in the Bureau of Mines laboratories, as well as most of the published data of other investigators. Parts II, III, and IV will contain chapters on thermodynamic properties and metallurgy. Part V comprises the bibliography and index.[2]

The experimental work reported herein was done in cooperation with the University of Missouri School of Mines, Rolla, Mo.; the University of Minnesota, Minneapolis, Minn.; the Carnegie Institute of Technology and the Metallurgical Advisory Board, Pittsburgh, Pa.; and the University of Nevada, Reno, Nev.

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[2] Throughout parts I to IV, numbers in parentheses refer to items in this bibliography, and page numbers to those in the reference cited.

CHAPTER 1. PHYSICAL PROPERTIES AND PREPARATION OF METALLIC MANGANESE

By R. S. Dean[3]

PURE MANGANESE

Although manganese is one of the commoner metals, as judged by the distribution of its compounds in the earth's crust, comparatively little is known about the element itself, due to the difficulty of obtaining the metal in a high state of purity. Manganese of more than 99 percent purity has been available only since the introduction of vacuum distillation in the high-frequency furnace by Gayler (107) in England and Friauf (98, 255) in this country.

Table 1, from Gayler (107), gives the analyses of distilled manganese.

TABLE 1. - Analyses of Distilled Manganese, Percent

Sample	Sulphur	Silicon	Carbon	Iron	Aluminum	Phosphorus	Magnesium	Manganese
A	-	Trace	0.013	Nil	Nil	-	-	-
B	-	Nil	.01	do.	do	-	-	-
C	-	0.021	-	do	Tr.	-	-	-
D	-	.005	-	do	do	-	-	-
E	-	.11	-	do	do	-	-	-
F	0.012	.06	.01	Under 0.04		0.01	Nil	1/99.5

1/ By difference, 99.87.

NOTE.- On similar samples the nitrogen content was found to be 0.01 percent or less.

Manganese of this purity as distilled or after vacuum melting is reported by both Gaylor and Friauf to be silver-gray and very brittle. It is hard enough to scratch glass and will not tarnish in air.

The question whether the absolutely pure metal is ductile must remain unanswered. Corson (59) believes that the pure metal is ductile. He bases this opinion on the fact that Zhemchuzhny was able to obtain ductile manganese and draw it to fine wires by the simple expedient of adding about

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[3] Chief engineer, Metallurgical Division, U. S. Bureau of Mines.

3 percent copper to the aluminothermic product. Corson suggests that the copper brings the silicides, aluminides, nitrides, and carbides into a less harmful form of distribution.

Dyson (78) describes manganese prepared by electrolysis of aqueous chloride solution as having a faint pink tinge and being soft and easily polished. The annual report of the National Physical Laboratory for 1924 states that the product of such an electrolysis is subject to disintegration and oxidation, indicating that it is essentially different from the distilled product. Campbell (44) found electrolytic manganese brittle even when annealed to remove hydrogen.

These differences with regard to the properties of metallic manganese find an explanation in the existence of several allotropic forms of the element. Gayler (107) has found four transformations accompanied by marked thermal phenomena occurring at the following temperatures.

	°C.		°C.
(1)	1,191 ± 3	(3)	742 ± 1
(2)	1,024 ± 2	(4)	682 ± 1

Microscopic examination indicates that transformation 3 is accompanied by a change in crystal structure, while no such change is apparent with regard to transformation 4. Moreover, one of these transformations is accompanied by a marked change of volume, which is so great that an ingot formed by melting the distilled metal in vacuo is cracked extensively on cooling.

Westgren and Phragmen (388) have shown by X-ray spectrometry that electrolytic manganese is tetragonal with

$$\underline{a} = 3.774 \pm 0.003\underline{A};\ \underline{c} = 3.533 \pm 0.003\underline{A};\ \underline{c}/\underline{a} = 0.937.$$

Since the manganese produced by distillation has a cubic lattice, this explains sufficiently the difference of properties between distilled and electrolytically deposited manganese without recourse to assumed effects of impurities. The investigations of Perrson and Öhman (303) show that by alloying manganese with small amounts of copper and quenching from temperatures above 1,160° C. structures showing the tetragonal lattice of electrolytic manganese may be obtained. By varying the amount of copper and extrapolating to pure manganese the parameters of this γ manganese are obtained as

$$\underline{a} = 3.776 \pm 0.005;\ \underline{b} = 3.525 \pm 0.008;\ \underline{c}/\underline{a} = 0.934.$$

By comparing these with the parameters given by Westgren and Phragmen quoted above, it is evident that this high-temperature form of manganese is identical with the electrolytic form. Perrson and Ohman also found that this high-temperature form, when stabilized by small amounts of copper, is soft and ductile, which is in agreement with the observations of Zhemchuzhny.

The γ form of manganese, whether formed by electrolysis or quenching is rapidly transformed to α manganese when heated to 150°C. and even at room temperature is completely changed after a few weeks. This instability is doubtless responsible for the variation in properties described.

The transformation found thermally by Gayler (107) at 1,024°C. was not found by Perrson and Öhman (303) in their study of crystal form as revealed by X-ray methods. Neither was it found in the further work of Gayler (108).

According to Schulze (343), commercial manganese is frequently found to be a mixture of the α form with another very complicated structure. By heating this commercial manganese to 1,000°C. and quenching, X-ray studies show only the second complicated structure which has been called β manganese. This structure is a cubic lattice with 20 atoms to the unit cube, while α manganese has 56 atoms to the unit cube. The transformation $\alpha \rightleftarrows \beta$ is identified with the thermal change found by Gayler at 742°C. The transition at 682°C. is unaccompanied by a change in structure. Bradley (33) suggested that the two forms of manganese occur in a state of isodynamic isomerism within the temperature interval 650°-850°C. and that the equilibrium gradually shifts over to the β modification as the temperature is raised. Perrson and Ohman (303), however, found no trace of β manganese in the pure metal quenched from 730°C., while that quenched from 760°C. showed only faint α lines.

Bernal (23) has proposed that both α and β manganese are alloys and points out that their structures are such that if manganese were not known to be an element they would certainly be counted as alloy structures. β manganese is, in fact, isomorphous with $AlAg_3$. The sudden break in the atomic volume curve at manganese is adduced as further evidence that both α and β manganese may be, in fact, alloys. Additional support for this view is found in the peculiar behavior of manganese during work hardening by the pendulum tester. Sandifer (334) reports that the hardness falls from 77 to 30 as the pendulum swings some 40 times. This effect may be due, however, to cracking.

In summary then, manganese exists in three well-defined crystalline varieties[4]:

α = 56 atoms per unit cube; a = 8.89; stable below 742°C.
β = 20 atoms per unit cube; a = 6.28; stable 742° - 1,191°C.
γ = tetragonal a = 3.774 ± 0.003A; stable 1,191°-M.P.
c = 3.533 ± 0.003A.
c/a = 0.937.

The α and β forms are brittle at room temperatures. The β form becomes slightly malleable at 900°C. The γ form is soft and ductile. By electrolysis the γ form is obtained in a metastable state.

The melting point of manganese is given by Gayler as 1,244 ± 3°C., which is some 20° higher than that obtained by earlier investigators and is presumably to be accepted as accurate, because of the high purity of Gayler's sample, although this value stands otherwise unsupported. The vapor pressure, specific heat, and other thermodynamic properties of manganese are discussed in part II, chapter 5.

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[4] Values for the parameters taken from Ewald and Hermann's Struckturbericht.

The specific gravity is variously given, depending on the sample used. Figures ranging from 7.05 to 8.01 have been recorded. The true density of α manganese from X-ray measurements is given by Preston (309) as 7.44. The atomic volume of manganese is given by Goldschmidt (118) as $14.85 \cdot 10^{-24}$.

The volume change on solidification of manganese has been investigated by Matsuyama (245), who found that a contraction of 1.7 percent, a comparatively small shrinkage, occurs on solidification. The figure for copper is 4.2 aluminum 6.26, silver 5.00, and iron 5.5. For detailed consideration of manganese in various states see chapter 5.

The initial linear compressibility of manganese is given by Bridgeman (40) as $2.6 \cdot 10^{-7}$. This figure is about normal with respect to the position of manganese in the periodic table.

The electrode potential of presumably α manganese analyzing 99.6 percent manganese, prepared by electrolysis of manganese salts into a mercury cathode and subsequent distillation of the mercury and melting in hydrogen, is given by Royce and Kahlenberg (321) as 1.45 volts, based on the value +0.560 for the normal calomel electrode. The magnitude of this potential is confirmed by the replacement of zinc, cadmium, iron, cobalt, nickel, lead, hydrogen, copper, and silver from their solution by metallic manganese.

The atomic electrical conductance of manganese is given by Kraus (214) as 0.6561. This and most other figures in the literature for the electrical conductance of manganese seem to be based on the work of Kuh (222). Stated in terms of specific resistance, Kuh's value is $82 \cdot 10^{-6}$ ohms per cubic centimeter at room temperature. Hume-Rothery (174), however, gives $5 \cdot 10^{-6}$. No data are available for the temperature coefficient.

The magnetic susceptibility of manganese is given by the International Critical Tables as $9.9 \cdot 10^{-6}$ at 18°C. More recent figures obtained by Mary H. Wheeler (according to a letter from Prof. L. W. McKeehan, Yale University), are $10.58 \cdot 10^{-6}$ for α manganese and $9.70 \cdot 10^{-6}$ for β manganese. Accordingly, it is one of the more strongly paramagnetic metals. Kuh states that manganese fused in hydrogen is ferromagnetic. At $H = 12,000$ δ 2.2; $H_c = 670$; and $d = 7.24$. (The δ/-H curve for this manganese is given in the International Critical Tables, vol. 6, p. 409, fig. 47.)

Freeze has confirmed Kuh's findings concerning the ferromagnetism of manganese fused in hydrogen, but found that electrolytic manganese or films of manganese prepared by sputtering in hydrogen were not ferromagnetic.

Oschenfeld (286) finds that manganese is made ferromagnetic by heating above 1,000°C. in nitrogen, whereby a solid solution of nitrogen in γ manganese is formed which is stable at room temperature.

Preparation of Metallic Manganese

Manganese is prepared commercially by heating manganese oxide with aluminum. Gayler (107) reports that if Mn_3O_4 is used it can be more easily ignited and better results obtained. Hadfield (140) gives the analyses of commercial metallic manganese shows in table 2. This method is due to Goldschmidt and Vautin (117).

TABLE 2. - Analyses of Commercial Metallic Manganese, Percent

Manganese ..	90.35	90.50	92.20	95.50	96.00	[1] 97.85
Carbon	1.18	.78	1.04	.08	.06	.025
Silicon	.92	.49	4.96	1.40	.60	.64
Sulphur	-	-	-	-	.208	-
Phosphorus .	.27	.30	0.36	-	.068	-
Aluminum ...	-	-	-	-	1.03	.28
Iron	-	-	-	-	.78	.75

[1] This was a special high-grade manganese from Thermit, Ltd.

Debuigne, in British Patent 221233, August 31, 1923, claims that the addition of oxides or hydroxides such as $Ca(OH)_2$ to the aluminothermic mixture lowers the reaction temperature and prevents reduction of SiO_2.

The electrodeposition of manganese may be accomplished from either sulphate or chloride solutions in water provided sufficient ammonia is present to neutralize the acid formed (91).

According to Allmand and Campbell (5) the best conditions for the electrodeposition of pure manganese are the electrolysis of a solution containing manganous and ammonium sulphates separated by a diaphragm from the anolyte (ammonium sulphate solution) the hydrogen ion concentration being kept at 10^{-6}-10^{-8} by regulated additions of sulphuric acid or ammonia. The temperature is 30°C., the cathode current density 10-15 amp./dm^2. The rotary aluminum cathode has a burnisher pressing against it.

Electrolytic manganese is the unstable γ modification, the properties of which have already been described. Its density is considerably lower than for the distilled metal. Campbell gives the density as 7.034.

Electrolysis from fused silicates containing some iron gave only iron with 0.8 percent of manganese (45, 271).

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CHAPTER 2. MANGANESE IN NONFERROUS ALLOYS

By R. S. Dean[5]

MANGANESE AS A SCAVENGER

Manganese has been said to be the universal cure-all and tonic for the metallurgist. It appears in the formula for almost every alloy that has been patented or described in detail. The full explanation of this effect of manganese is by no means available; however, the position of manganese as a transition element between the highly electropositive elements and the heavy metals apparently makes it valuable.

Thus manganese is sufficiently electropositive to have a high affinity for sulphur and a sulphide of essentially nonmetallic properties, yet the metal is not too volatile or easily oxidized to be readily used as an addition. Furthermore, manganese forms solid solutions with most metals so that the excess added does not occur in a particularly harmful form. The relative affinity between metals and sulphur is given by Parravano and Malquori (292) in the following list: $Ag < Pb < Ni < Fe < Cu < Mn$.

Moreover, the fact that manganese sulphide is insoluble, whereas heavy metal sulphides are somewhat soluble in metals enables the desulphurizing reaction to proceed to completion. The physical properties of the manganese sulphide formed are also important. According to Picon (304) it vaporizes without decomposition at 1,375°F. so that when it appears as a free phase in nickel and copper alloys, considerable loss by vaporization is to be expected. Manganese sulphide is soluble in silicate slags. The system $MnS - MnSiO_3$ has been investigated by Woleskow (394) and by Glaser (114). Both investigators report a eutectiferous system. If the alloy is melted under a silicate slag the manganese sulphide may therefore find its way into the slag.

COMMERCIAL ALLOYS CONTAINING CONSIDERABLE PERCENTAGES OF MANGANESE

Only the alloys of manganese with copper and aluminum have great importance commercially.

System Copper-Manganese

Since the axial ratio of tetragonal manganese approaches 1 with increasing copper content manganese can form solid solutions throughout the whole range of composition with copper, which has a face-centered cubic structure. In general, the mechanical properties of the copper-manganese alloys up to

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[5] Chief engineer, Metallurgical Division, U. S. Bureau of Mines.

30 percent manganese change continuously with increasing manganese content. All these alloys, according to Patterson (296) are face-centered cubic with a increasing from 3.60-3.70A (296). According to Corson (59) they may be melted in a graphite crucible without absorbing more than 0.2 percent carbon, which is not objectionable except for heavy drawing. According to the same author, the hardness of such carbon-containing alloys is sharply dependent on the state of subdivision of the manganese carbide. By quenching from 800°C. and reheating to 400 to 450° for 24 hours, a hardness of 125 may be obtained compared to about 40 for the annealed alloy.

Manganese raises the annealing point of copper, hence alloys containing 4 to 5 percent manganese are used for turbine blades; 4 percent manganese is also used in copper for locomotive fire-box plates and stays, where its principal function seems to be to insure complete deoxidation, with consequent freedom from brittleness caused by reducing gases.

The greatest interest in the copper-manganese system, however, arises from the fact that the alloys containing 12 to 17 percent manganese have a very low temperature coefficient of electrical conductivity. Such alloys, known as manganin (8 to 12 percent manganese), have been described by Bash (16).

The low melting point (about 850°C.) of the alloys containing 20 to 35 percent manganese and the strong but chemically neutral skin of oxide covering the molten alloy have led Corson (59) to suggest their use as die-casting alloys. U. S. Patent 1671408 covers alloys containing 15 to 25 percent manganese and 1 to 3 percent phosphorus and silicon.

The high-manganese members of the copper-manganese system are especially interesting, because the addition of a few percent of copper enables the γ form of manganese to be obtained at room temperature by quenching. Since, according to Persson (301), no solubility of copper in α or β manganese can be detected, the copper must be rejected as a separate phase when the gamma form of manganese breaks down to the α and β.

Ternary Copper Alloys Containing Manganese

These alloys include special brasses, manganese bronze, and Heusler alloys.

In general, manganese acts as a substitute for copper when added to brass, so that alloys containing 30 percent zinc and 10 percent manganese would have properties similar to those of cartridge brass. Such alloys have not, however, found commercial use. The so-called manganese bronzes, containing about 1 percent manganese in addition to iron, silicon, tin, or aluminum, owe their value to the introduction of other elements, notably iron, with the manganese. A brass has recently been developed for hot-pressing, in which silicon is added with the manganese to such an extent that plainly visible crystals of hard manganese silicide are embedded in a body of regular manganese bronze.

The alpha-phase boundary of the ternary system copper-silicon-manganese has been carefully determined by C. S. Smith (351), who finds that the solubility falls to less than 0.5 percent at 450°C., when more than 4 percent manganese or silicon is present.

Another most interesting series of ternary copper-silicon-manganese alloys are the so-called Heusler alloys. These are alloys of copper with 7 to 11 percent aluminum and 20 to 30 percent manganese. By quenching these alloys from a high temperature and drawing at 600° to 700°C. followed by quenching they acquire ferromagnetic properties.

The structure of these Heusler alloys is given by Elam (81) as follows:

Mn	Al	Cu	
27.7	5.7	66.6	Face-centered, a = 3.7.
28.2	8.6	63.2	Body-centered, a = 2.975.
27.1	12.3	60.2	Body-centered , which is cubic, 58 atoms per unit cell.

No commercial uses have been found for these alloys.

Silver can be substituted for copper in Heusler alloys, according to Potter (308), the silver, aluminum and manganese alloys being ferromagnetic. The best alloy is 5 atoms of silver, 1 of manganese, and 1 of aluminum; it has a saturation intensity of 70 units per cubic centimeter or somewhat less than Heusler alloys.

The special brasses containing nickel and manganese are said to have low corrodibility. A typical composition as given by LeThomas (232) is Cu, 53.2 percent; Zn, 38.8 percent; Ni, 4.46 percent; Mn, 3.0 percent; Fe, 56 percent (31).

Commercial manganese - aluminum alloys contain 0.5 to 3.0 percent manganese. Manganese is also used as a constituent of duralumin-type alloys where, according to Corson (59), it always forms the compound Al_3Mn. This, however, has not been confirmed by Dix (72). According to Meissner, manganese is not indispensible but up to 0.6 percent manganese considerably increases strength.

The alloy of aluminum with 2.5 percent manganese, 2.25 percent magnesium, and 0.2 percent antimony has been found to be particularly effective in withstanding corrosion of sea water. It is known in Germany as K. S. Seewasser.

According to Haas (132), an alloy of 2 percent manganese is to be recommended for sand castings. It has a tensile strength of 30 kilograms per square millimeter and an elongation of 5 percent. For rolling, the alloy should contain 1.25 percent manganese, which has a tensile strength of 29-81 kilograms per square millimeter, and an elongation of 25 to 1 percent, depending on mechanical and heat treatment.

The structural details of the aluminum-manganese system have been investigated by Bradley and Jones (34). They found that a small amount of aluminum added to manganese lowers the β and γ transition point of manganese to such an extent that the γ form is stable at room temperature. Seven different phases are found to exist.

Manganese Alloys of Minor Commercial Importance

The magnesium-manganese alloys have been investigated by Schmidt (338), who concluded that the manganese appeared as an intermetallic compound. Bakken and Wood (13) report that manganese is soluble up to at least 3.2 percent. Pearson (298) concludes from microscopic investigations that the solid solubility extends beyond 2.7 percent.

Nothing seems to be known on the physical properties of these alloys. Manganese is added to magnesium-aluminum alloys as a corrosion inhibiter.

Investigations of the nickel-manganese alloys have been summarized by Pilling and Kehlgran (305), who give them as a nearly continuous series of solid solutions with a minimum melting point at 1,000°C. A heterogeneous range between 41 and 70 percent manganese is suggested, but little is known of its exact nature.

Blumenthal, Kussmann, and Scharnow (27), in a more recent investigation of the alloys of manganese and nickel and of manganese and cobalt have reported that both alloys are heterogeneous. According to Kaya and Kussman (194) a distribution of manganese atoms in the nickel lattice corresponding to the formula Ni_3Mn makes alloys strongly ferromagnetic.

The mechanical properties of the nickel-manganese alloys have been investigated by Mudge and Luff (265). They conclude that manganese up to 4.63 percent results in a definite increase in strength, toughness, and hardness of the nickel alloy, with practically no decrease in ductility. The nickel-copper alloys are similarly affected. Alloys of 96 percent nickel and 4 percent manganese are used for the points of spark plugs.

The manganese-zinc alloys have been investigated by Ackermann (1), who found that zinc alloys with more than 3 percent manganese are brittle. According to Parravano and Montoro (293) at least three solid-solution phases are present in zinc-manganese alloys up to 23.3 percent manganese. Up to 0.98 percent manganese the η phase has a hexagonal lattice like that of zinc. Above this amount the ε phase forms, having a hexagonal lattice different from zinc and finally a γ phase with a body-centered cubic lattice forms.

Lead and manganese do not alloy, but the addition of manganese to alloys of lead, antimony, and tin has been covered in British Patent 309399, January 9, 1928. It is suggested as having value as a bearing metal.

The system silver-copper-manganese has been investigated by Keinert (199). Two series of solid solutions are formed. The silver-rich alloys can be hardened at 280°C. after quenching from 750°C.

CHAPTER 3. COMPOUNDS OF MANGANESE

By R. S. Dean[6]

METALLIC COMPOUNDS

G. Haag (130) has pointed out that the compounds of transition element such as manganese with the metalloids are metallic. The metallic condition appears to be connected with the small dimensions of the metalloid atoms. These metallic phases have embedding structures. In such structures the metalloid atoms are always so arranged as to yield a maximum coordination number, hence the face-centered cubic lattice is frequently found. Some compounds of manganese with boron, phosphorus, tin, and arsenic are ferromagnetic. Perrson's (302) suggestion that ferromagnetism is connected with orientation of the manganese atoms in a face-centered structure is in general agreement with these facts.

Manganese-tin compounds have been investigated by Potter (307), who finds that $SnMn_4$ and $SnMn_2$ are ferromagnetic. The Curie point of $SnMn_4$ is 150°C. and the saturation value about 100 units. The Curie point of $SnMn_2$ is 0° and the saturation value 470 units or virtually that of nickel.

The arsenide and antimonide of manganese have been investigated structurally by DeJong and Willems (65), who find that they have the FeS structure with a = 37.4, c = 5.75 for MnAs, and a = 4.14, c = 5.90 for MnSb. Bates (17) has investigated the magnetic properties of the arsenide and phosphide.

The nitrides of manganese have been investigated in some detail by Haag (131). From 0 to 2.2 percent N. the δ phase is stable at high temperatures but decomposes in α manganese and the ε phase between 600° - 400°C. The manganese atoms in the δ phase are arrangod in a face-centered tetragonal lattice with a = 3.765, c = 3.684. The ε phase exists from 6 - 6.65 percent nitrogen at 400°C. In this phase the manganese atoms form a face-centered cubic lattice. The unit cell contains 4 manganese atoms and 1 nitrogen atom. At temperatures above 500°C. the ε phase field is enlarged toward smaller nitrogen contents.

The telluride of manganese ($MnTe_2$) has a pyrite structure a = 6.943, according to Oftedal (281).

Manganese forms two sulphides (MnS and MnS_2) known mineralogically as alabandite and hauerite. The monosulphide is particularly important in metallurgy. According to Schneiderhöhn (340), it has a structure analogous to rock salt, with a = 5.21. It has a very high index of refraction, N_{Li} = 2.70. Its most interesting characteristic is its ability to behave both as a metallic and nonmetallic substance. It is, for example, soluble in molten silicates as well as in molten sulphides. The system $MnS-MnSiO_3$ has already been mentioned. Its equilibrium with iron sulphide has been investigated by Shibata (346)

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Manganese sulphide therefore has the unusual property of being soluble in both metallic and nonmetallic melts. The question at once arises as to its distribution between such melts, but no data are available.

Other very peculiar properties are reported for manganese sulphide; thus Picon (305) reports that molten MnS will dissolve graphite. Krekel (216) reports that manganese sulphide and iron form a eutectic.

NONMETALLIC COMPOUNDS AND THEIR USES

Oxides of Manganese

Manganese forms four oxides--MnO_2, Mn_2O_3, Mn_3O_4, and MnO. The equilibrium relations and natural occurrence of these oxices are discussed elsewhere in this bulletin. Two more states of oxidation are represented in the salts of manganese, MnO_3 and Mn_2O_7.

The oxide MnO is formed when any of the higher oxides are reduced by hydrogen below 1,200°, is pale green, and melts at 1,605°C. It crystallizes in a cubic lattice of the NaCl type, with A_0 = 4.40 A°. MnO is isomorphous with CaO, CdO, MO, and MgO but exhibits only partial solid miscibility with them. Solid MnO dissolves 31 percent MgO and 21 percent CdO, while MgO and CdO dissolve 26 percent MnO. Solid MnO dissolves about 9 percent CaO (269, 270).

The system MnO - FeO has metallurgical importance and has been studied by Andrew and Maddocks (9).

The compound $MnFe_2O_4$ can be prepared by calcining the mixed hydroxides at 800°C. It is cubic, with *a* = 8.515 and a calculated density of 4.965 (Passerini) (294).

MnO is soluble in acids and also in ammonia.

The oxide Mn_3O_4 is formed when the other oxides of manganese are heated in air above 940°. Obtained in this way it is brownish or reddish in color but when occurring naturally as the mineral hausmannite it is black.

Manganic oxide (Mn_2O_3) is formed by igniting the dioxide, nitrate, carbonate, or oxalate below 940°C. It is a brown powder which shows a cubic crystal structure of the corundum type--*a* = 9.391 (Wretblad) (395). It forms solid solution to a limited extent with Fe_2O_3. Mn_2O_3 behaves with regard to acids as if it were MnO, MnO_2.

MnO_2 has only feebly basic properties. When heated with sulphuric acid manganese dioxide evolves oxygen and passes into solution, manganic sulphate being formed. Brown solutions of the disulphate can, however, be formed by anodic oxidation of manganous sulphate. The tetrachloride is also unstable but may be produced as the double salt $MnCl_4 \cdot 2\,KCl$ by passing HCl into a solution of $KMnO_4$ in glacial $HC_2H_3O_2$.

The acidic character of MnO_2 is more pronounced than the basic. When hydrated manganous oxide is oxidized by air in the presence of $CA(OH)_2$ calcium manganite is formed.

MnO_2 is readily soluble in acids with the addition of a reducing agent, such as SO_2. Except as a source of manganese, none of the oxides but the dioxide have any commercial uses.

The principal use of the dioxide is as a depolarizer in dry batteries. For this purpose high-grade MnO_2 is required. Both artificial and natural products are used. Apparently the hydrated form gives better results (193, 238).

Manganese chloride ($MnCl_2$) is obtained as a byproduct in the preparation of chlorine from MnO_2. It is isomorphous with $FeCl_2$, and its purification by crystallization istherefore impractical.

A mixture of manganous chloride and ammonium difluoride has been recommended by Ferrari (93) for degasifying aluminum (355).

Manganese carbonate ($MnCO_3$) occurs naturally as rhodochrosite. It is rhombohedral ($a = 5.84$, $\alpha = 47^\circ 20$) and according to Kreiger (215) forms a continuous series of solutions with calcium carbonate. It is also isomorphous with iron carbonate and magnesium carbonate, and such mixtures occur naturally as oligonite. The carbonate is formed by the addition of the alkali carbonates to a solution of manganous salts.

Manganese Sulphate

This salt is used as a drier in light oils and especially as a component of fertilizers. (Mazzuchelli) (257). The salt crystallizes from water in several hydrated forms. The anhydrous salt takes up water from the air, and the higher hydrates lose water; the monohydrate, however, is stable in air and is therefore best suited to shipping. It is obtained by heating the higher hydrates at 100°-200°C. (Krepelk and Rejha) (217).

Manganates and Permanganates

The higher oxides of manganese - MnO_3 and Mn_2O_7 - are acidic and occur as salts formed by oxidation of manganous salts. When MnO_2 is fused with sodium or potassium carbonate or hydroxide manganates are formed. Manganates form green solutions stable when alkaline but break down when neutral or acid, forming the permanganate and MnO_2. In commercial preparation of permanganate, oxidation to the heptavelent state may be obtained by chlorine or electrolysis.

Manganese Ores in Ceramic Industries

Glass Making

Practically all the raw materials used in glass contain some iron, usually in the form of ferric oxide. The iron, when present even in small quantity, imparts to the glass a pale green color that increases rapidly in intensity as the iron content increases. If a colorless glass is desired this green must be removed by some decolorizer. Manganese, selenium, cobalt, and nickel are the most common decolorizers in use, and of these manganese has been most widely employed because it permits easy control of the color. In using selenium and nickel the quantity must be carefully controlled, but these latter substances are desirable, especially in window and plate glass, because glass decolorized with manganese often changes to a pink on exposure to the light. A decreasing quantity of manganese is being used by makers of tank glass, its place being taken by selenium.

The quantity of manganese used varies considerably, depending on the character of the glass, the method of its manufacture, the iron content of the raw materials, and the character of the manganese ore used. Each manufacturer has his own ideas on this subject. The quantity used is figured in terms of pounds of manganese dioxide per thousand pounds of sand, which constitutes 50 to 75 percent by weight of the entire batch. The temperature employed in the glass-making process influences the quantity of manganese dioxide used since, because of volatilization, more manganese is necessary at higher temperatures. The maximum limit is 10 to 15 pounds of manganese dioxide per thousand pounds of sand, and the minimum may be 2 to 2½ pounds.

Chemistry of Use of Manganese in Glass-Making Process. - When other coloring ingredients are absent, compounds of manganese produce pink, purpose, and violet hues, according to the chemical nature of the glass. Manganese dioxide neutralizes the green color caused by iron compounds. Used in excess it imparts an amethyst tint, and when used in considerable excess the color is so dark as to appear black.

Neutralization of the iron tint by manganese dioxide is explained by some chemists as a physical effect, and by others as a purely chemical one. The green tint is due to the presence of ferrous silicate. Some chemists think that this green compound is oxidized to the ferric silicate, which is an almost imperceptible pale straw-yellow. According to this view, the oxidizing agent used must not decompose completely at high temperatures, and manganese dioxide seems to be the most available compound fulfilling this condition. At red heat the dioxide loses one third of its oxygen, leaving the tetraoxide (Mn_3O_4), which at still higher temperatures is an oxidizing agent.

Red lead and other oxidizing agents have not this decolorizing power, hence some chemists have thought that the decolorization by MnO_2 is purely physical and is not due to oxidation or chemical reaction. It is possible, however, that other compounds may lose their oxygen at too low temperatures to be effective as oxidizing agents.

Specifications for Manganese Ore Used in Making Glass. - Before the World War the ordinary specifications for manganese ore used in glass making were 85 to 90 percent manganese dioxide and less than 1 percent metallic iron. Outside of these two ingredients, each manufacturer has his own requirements. Special glasses may require ore carrying more than 90 percent manganese dioxide and less than 0.5 percent iron. The higher the manganese content and the lower the iron, the better the ore is for glass making. In general, the grades of ore are similar to those used in making dry cells. Obviously, siliceous pyrolusite is not objectionable but carbonaceous pyrolusite is.

Manganese ore for glass making is sold in powdered, granulated, or lump form. There are objections to the lump form because of the time required to melt it into the batch. Powdered ore is used principally when the batch is melted in pots; lump or granular ore is used when melting is done in tanks.

Before the war high-grade pyrolusite for glass making and other chemical purposes was imported from Russia, Saxony, Japan, Nova Scotia, and other foreign countries. As the war progressed such ore became scarce; in consequence, specifications were relaxed, and low-grade ores were purchased. During the war some excellent domestic ore was developed and found a ready market.

Other Ceramic Uses

Another use for manganese ore in glass making has developed in the last few years, namely, for producing black glass used for ornamental purposes. About 3 percent of ore is added to the batch in making this opaque glass.

Pyrolusite is added to the constituents of glazes and enamels to produce purple tints. Black enamels are those containing manganese. Manganese oxide is also used in brick making. Manganese has also been recommended for improving the color of brick (39).

Use of Manganese Salts in Driers

Definition

Driers are substances, generally metallic oxides or their compounds, that are added to linseed or other drying oils at high or low temperatures to make them capable of readily absorbing oxygen from the air, or of drying by its action. Some chemists consider the action to be catalytic, the manganese compound acting as a catalyzer or carrier of oxygen. The principal manganese compounds used as driers are manganese sesquioxide (Mn_2O_3), pyrolusite (MnO_2 --also known in the trade as dioxide, binoxide, or peroxide), manganese hydrate, manganese sulphate, manganese borate, manganese resinate, manganese linoleate, manganese oxalate, and possibly other salts. Certain corresponding double salts of manganese and lead are often used.

Manganese Dioxide

Manganese dioxide, extensively used as a drier, is marketed in two forms, the natural and the artificial. The natural mineral pyrolusite is simply ground to a powder with water and then dried. The mineral is essentially a peroxide, a class of substances containing more oxygen then is required to satisfy the valence of the metal present. This extra oxygen is loosely combined and readily enters into combination with oxidizable bodies. This feature of manganese compounds makes them useful in oil boiling because the oxygen combines with the oil, oxidizing it, while some of the manganese dissolves and forms a compound with the linoleic acid of the oil. In consequence of this action manganese compounds are powerful driers. The quantity of manganese dioxide added in the process of boiling is small, not more than a quarter of a pound to a hundredweight of oil to get the best results. The use of the black dioxide, however, tends to darken the oil.

Manganese Borate

Manganese borate is perhaps the least objectionable of all manganese salts used as drying agents, although the black oxides are used more. To make the borate, 1 part of manganese sulphate is dissolved in 10 parts of distilled water, and a little of this solution is added to some soda solution to determine whether any iron is present. If pure, the manganese sulphate solution is added to the hot borax solution as long as a precipitate forms. The precipitate is filtered, washed with hot water, and dried.

Manganese Resinate

Resinates, formed by the combination of resin or rosin with certain metallic oxides, are much used in making varnish and paint and with the exception of the linoleates are most readily soluble in linseed oil. Manganese resinate is made as follows: Soda ash is dissolved in water, and the solution is boiled with steam; the proper proportion of light coarsely powdered rosin is added, then more soda ash. The clear solution is run into a clear manganese chloride, the resinate separating as a white flocculent precipitate, which is filtered, washed, and dried.

Manganese Linoleate

Manganese linoleate is prepared by pouring a solution of a soap, made by boiling linseed oil and caustic soda, into a solution of manganese chloride or manganese sulphate. The dark-brown plasterlike mass is susceptible to oxidation. When exposed to air the surface becomes covered with a hard, rather insoluble, protective skin. The material should therefore be kept in tightly closed vessels. It acts both as a bleaching agent and a drier for linseed oil. One pound, mixed first with 5 pounds of linseed oil and the whole poured into 10 gallons of linseed oil at 250° F. gives a good drying oil.

The double resinates and linoleates of manganese and lead are also in use.

Manganese Oxalate

Manganese oxalate is prepared by precipitating manganese salts with oxalate of soda or potash or by treating manganese hydrate or carbonate with oxalic acid. One of the advantages of the oxalate is said to be that it decomposes during oil boiling. The manganese dissolves in the oil in combination with linoleic acid, and the oxalic acid is decomposed with evolution of carbonic acid. One fourth to one half pound may be used per hundredweight of oil.

CHAPTER 4. OCCURRENCE AND ORE-DRESSING POSSIBILITIES OF ORES OF MANGANESE IN THE UNITED STATES

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By Fred D. DeVaney[7] and Will H. Coghill[8]

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INTRODUCTION

Present-day metallurgical practice requires a large amount of manganese, of which the steel industry is the largest consumer. The chemical and ceramic industries also need manganese-bearing ores. These demands are so great that the consumption of manganese by our industries far exceeds our domestic production. This condition can in part be attributed to the fact that, although large amounts of manganese oxide and carbonate ores occur in the United States, relatively little is of the required grade. Concentration would be necessary. Lack of a sufficient supply of high-grade manganese ore and of well-developed concentration processes places the nation in a vulnerable position when large quantities of manganese must be imported for use in the manufacture of steel. An economical and efficient means of concentrating the low-grade oxide and carbonate ores would augment domestic production and reserves and would be a safeguard in times of emergency.

For about 2 years the United States Bureau of Mines, in cooperation with the Missouri School of Mines and Metallurgy, carried on at its Mississippi Valley Experiment Station, Rolla, Mo., an investigation of the manganese bearing ores of the country. In the course of this research ores from 116 mines or prospects in 20 States were examined and studied to determine their amenability to concentration by gravity processes, such as jigging and tabling, and by flotation and magnetic methods. Leaching processes, which are frequently placed in the ore-dressing category, are discussed in chapter 7.

In addition to determining amenability to treatment by the older well-known methods - gravity and magnetic concentration - an endeavor has been made to improve old methods and to devise means of treating ores that cannot be concentrated by methods now in use.

Outstanding results of this study include the development of flotation processes for concentration of oxide ores and carbonate ores and the application of better gravity-concentration methods in certain more important mining districts. The large amount of data assembled while samples from various districts were studied should prove of value in future, as they indicate the grade of concentrates that can be made.

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No attempt has been made to compute concisely the amount of ore in the various deposits or to estimate the cost of concentration processes. The tonnages of ore in many deposits are as yet uncertain and can be determined only by further exploration.

The costs of the processes mentioned are well known throughout the present milling industry, and the average will apply here.

MANGANESE DEPOSITS IN THE UNITED STATES

A survey of the literature shows that manganese ore is known to occur in about 300 districts scattered throughout 35 States. The size of the deposits and the manganese content of the ore vary greatly. Many deposits are small, containing only a few hundred or a few thousand tons, while others are known to contain ore that is measured by the millions of tons. The grade of ores in these deposits varies between wide limits; some contain only a small percentage of manganese, while others are of commercial grade without need of concentration.

A map and bibliography (147) of the manganese deposits of the United States, showing the widespread distribution and also giving a list of the references describing the various districts has been published. This map is reproduced as figure 1.

The ore samples for the investigation were obtained in several ways. Some were taken by Bureau of Mines engineers, and others were sent in by consulting engineers. Many of the samples, however, were supplied by the operators. When the investigation was begun operators were asked to furnish samples. This request met with a ready response. Of course, under some circumstances it would not be good engineering to allow the interested parties to do sampling, but in this instance a true representation of average-grade ore was not required; a knowledge of the general character of the ore was sufficient.

Of the 116 prospects or mines from which ores were examined 20 gave promise of yielding ferro-grade ore, either in the natural state or by concentration, while 43 fell in the class of ores suitable for other metallurgical purposes; thus, 63 properties had ore that was usable. Their phosphorus content would meet specifications, the ratio between manganese and iron was satisfactory, and the silica content was not too high or could be reduced by concentration. If time were available to re-examine these samples in the light of the knowledge acquired throughout the work, without doubt the list of promising ores would be increased. A list of the samples, grouped by States, is given in table 3. It shows how many could be used with or without concentration for the production of ferromanganese, for the manufacture of spiegeleisen, or for addition to the blast-furnace charge to supply manganese to the metal.

The authors do not intend to convey the idea that it would be economical to produce ore of the grade stipulated in the foregoing table from all the ores listed. Many deposits are small and would not justify the erection of a concentrating plant of any sort. Others have a grade of ore that makes them workable only when the price of manganese is high.

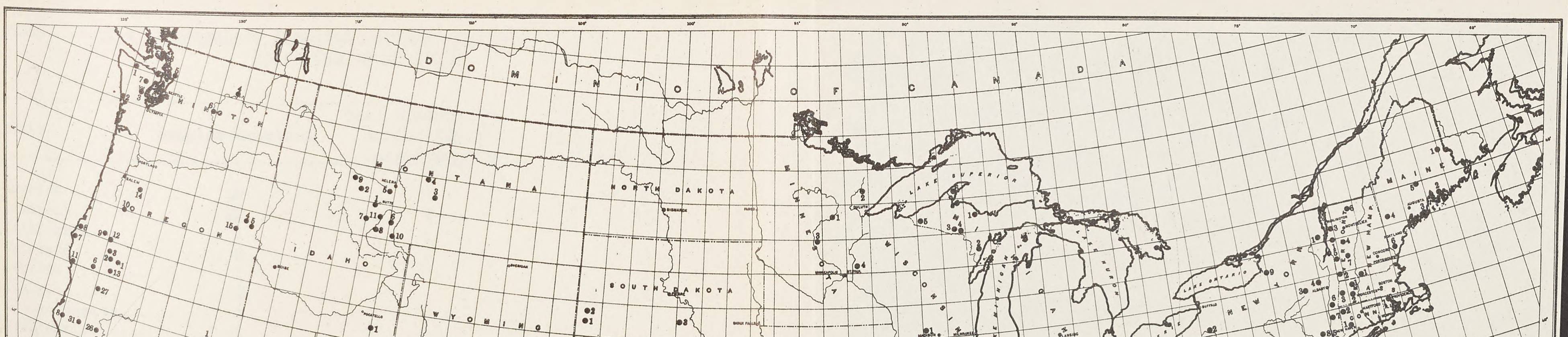
MANGANESE DISTRICTS
OF THE
UNITED STATES
DOMINION OF CANADA
MEXICO
GULF OF MEXICO
ATLANTIC OCEAN
PACIFIC OCEAN
WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
ARIZONA
COLORADO
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
ILLINOIS
MISSISSIPPI
MICHIGAN
INDIANA
KENTUCKY
TENNESSEE
ALABAMA
GEORGIA
FLORIDA
OHIO
WEST VIRGINIA
VIRGINIA
NORTH CAROLINA
SOUTH CAROLINA
PENNSYLVANIA
NEW YORK
MAINE
CUBA

Figure 1.

TABLE 3. - Ores of Manganese Examined, Grouped by States and Grade of Ore Which Can Be Recovered

State	Samples Examined	Ores suitable for production of ferromanganese	Ores suitable for other metallurgical purposes.
Arizona.........	18	4	5
Arkansas........	22	3	12
California......	1	-	1
Colorado........	2	1	1
Georgia.........	1	1	-
Idaho...........	2	-	1
Massachusetts...	1	-	1
Michigan........	1	-	-
Minnesota.......	7	-	4
Missouri........	2	-	1
Montana.........	8	3	1
Nevada..........	6	1	3
New Mexico......	7	1	4
North Carolina..	2	2	-
South Dakota....	1	-	-
Tennessee.......	12	2	4
Utah............	3	-	1
Virginia........	6	2	3
Washington......	13	-	1
West Virginia...	1	-	-
Total......	116	20	43

District and State:

Kingman, Ariz.
Batesville, Ark.
Leadville, Colo.
Cartersville, Ga.
Menominee, Mich.
Cuyuna, Minn.
Butte, Mont.
Philipsburg, Mont.
Franklin Furnace, N. J.

District and State:

Little Florida Mountains, N. Mex.
Silver City, N. Mex.
Las Vegas, Nev.
Chamberlain, S. Dak.
Northeast Tennessee, Tenn.
Blue Ridge, Va.
Woodstock, Va.
Olympic Peninsula, Wash.

Particular attention has been given to deposits with a record of high production or known to contain relatively large amounts of manganese-bearing material. These deposits are in the above districts, arranged alphabetically by States. Their ore-dressing properties constitute the basis of this report.

Ores from many other districts were studied, but lack of space prevents giving the experimental data on all but those which seem most important at present or which have attracted the most attention. Possibly some deposits not listed in this report will become large producers of manganese in the future; hence the absence of a report on certain districts is not to be considered as indicating an unfavorable attitude. For example, no report is given on the deposits in California, which was the second largest producer of manganese ores during the war years and undoubtedly can again produce much ore under favorable conditions. Due to the recent inactivity of the mines in that State representative samples were difficult to obtain.

CLASSIFICATION OF ORES OF MANGANESE

In this report the classification of ores containing manganese follows the system adopted by the Bureau of Mines in 1918. The term "manganese ore" is used to designate ores containing 35 percent or more manganese. Ores containing 10 to 35 percent are called "ferruginous manganese ores", while those containing 5 to 10 percent manganese are termed "manganiferous iron ores". Ores made up mainly of iron and containing less than 5 percent manganese are not classed as ores of manganese but simply as iron ores. The term "manganiferous silver ores" refers to ores that contain more than 5 percent manganese and enough silver to make them more valuable as a source of silver rather than of manganese. "Manganiferous zinc residuum" is a term applied to a byproduct resulting from the roasting of franklinite concentrates at Franklin Furnace, N. J.; it commonly contains 12 to 14 percent manganese.

PRODUCTION OF DOMESTIC ORES OF MANGANESE

Some idea of the relative importance of the various States as to the type and tonnage of manganese ores produced by each may be had from the figures in table 4, which shows the amounts of ore shipped from 1913 to 1930, inclusive. This table includes the tonnage of both fluxing ore and of the zinc residues produced at Franklin Furnace, N. J. It is felt that both types of material should be included, because the fluxing ore was used primarily for its manganese content, which serves a definite purpose, even though it is not recovered, and because the zinc residue which, though a byproduct from the smelting of zinc ores, is nevertheless the raw material from which most of the country's spiegeleisen is manufactured.

MANGANESE MINERALS

Manganese compounds occur in a variety of mineral forms widely distributed throughout the crust of the earth. From the commercial viewpoint by far the most important manganese minerals are the oxides. The world production of manganese outside of the United States comes almost entirely from the oxides. In this country the supply of the oxides is supplemented by the carbonate mineral rhodochrosite, from the deposits at Butte, Mont.

The manganese minerals (oxides, carbonates, silicates, and sulphides) will be described, after which the mineragraphic identification will be discussed. Table 5 gives the chemical composition and some physical properties of the more common manganese minerals.

TABLE 4. - Ores of Manganese, Including Fluxing Ore and Zinc Residues Shipped from Mines in the United States, 1913-30, Inclusive, in Long Tons[1]

State	Ore containing 35 percent or more Mn	Ore containing 10 to 35 percent Mn	Ore containing 5 to 10 percent Mn
Arizona........	52,971	37,448	21,449
Arkansas.......	61,419	108,479	147
California.....	2/ 63,328	359	---
Colorado.......	28,853	694,000	71,426
Georgia........	2/ 47,979	2/157,326	44,890
Idaho..........	5,337	1,839	---
Michigan.......	---	448,013	413,506
Minnesota......	---	2,715,446	7,088,693
Montana........	682,884	61,575	---
Nevada.........	2/ 31,618	2/724,086	7,987
New Jersey[3]....	---	2,069,000	---
New Mexico.....	22,650	349,479	166,996
Tennessee......	11,978	2/ 4,961	96
Utah...........	2/ 10,742	2/ 18,523	496
Virginia.......	66,458	51,787	52,400
Washington.....	16,275	---	---
Wisconsin......	---	---	1,819,172
Undistributed[4].	14,215	12,486	---
Total.....	1,116,707	7,454,855	9,687,258

[1] The production figures are taken largely from records published in Mineral Resources of the United States for the various years.

[2] Small additional production reported with "Undistributed".

[3] Zinc residues, production partly estimated.

[4] Includes production from States with small production and from States where permission has not been given to publish figures.

TABLE 5. - Chemical Composition and Some Physical Properties of More Common Manganese Minerals

Mineral	Composition	Assay, per-cent Mn	Specific gravity	Hardness	Color	Structure	Streak
Pyrolusite.....	MnO_2	60 to 63	4.73 to 4.86	2 to 2.5	Steel-gray or iron-black.	Radiating columnar but generally granular massive.	Black
Psilomelane...	$4 MnO_2$ Mn, Ba, K, O.nH_2	45 to 60	3.7 to 4.7	5 to 6	Steel-blue to black.	Massive, stalactitic, botryoidal.	Do.
Manganite......	$Mn_2O_3(H_2O)$	62.4	4.2 to 4.4	4	Steel-gray or iron-black.	Usually in radiating crystals.	Dark reddish brown.
Hausmannite.....	Mn_3O_4	72.1	4.73 to 4.86	5 to 5.6	Black to brownish black.	Generally crystalline.	Brownish black.
Wad.......	Hydrous mixture of oxides.	Variable.	3 to 4.3	1 to 6	Black or brown.	Amorphous or nodular.	Brown or black.
Alabandite.....	MnS	63.1	3.95	3.5 to 4	Iron-black to brown.	Usually granular massive.	Olive-green.
Rhodochrosite.	$MnCO_3$	47.8	3.45 to 3.6	3.5 to 4	Light to dark rose.	Usually cleavable; massive to granular.	Colorless.
Rhodonite.....	$MnSiO_3$	41.9	3.4 to 3.68	5.5 to 6.5	Rose	Commonly massive, cleavable to compact in imbedded grains.	Do.
Braunite.	$3Mn_2O_3$. $nMnSiO_2$	60 to 69	4.75 to 4.82	6 to 6.5	Black or brownish black.	Commonly in euhedral crystals, granular.	Brownish black.
Bementite.....	8 MnO_5. H_2O7SiO_2	31.0	3.1	6	Light gray or grayish brown.	Fine grained aggregate of plates or fibers.	Do.
Franklinite......	(Fe,Zn,Mn) O.$(Fe,Mn)_2$ O_3	10 to 20	5.0 to 5.3	5.5 to 6.5	Iron-black.	Massive, granular.	Reddish brown or black.

Oxide Minerals

The chief oxide minerals are pyrolusite, psilomelane, and manganite. Another oxide, hausmannite, although not uncommon has no economic importance except in two districts studied, the Batesville-Cushman, Ark., and the Olympic Peninsula, Wash. Franklinite is important in the Franklin Furnace, N. J. deposits. Wad is not a definite mineral but is a term in common use to describe earthy manganese-bearing material with a high moisture content. It is a mixture of manganese oxides.

Pyrolusite (MnO_2)

Pyrolusite, the manganese dioxide, contains 60 to 63 percent of manganese. Most varieties contain several percent of water. It is a black, opaque mineral with a metallic luster and is frequently soft enough to soil the fingers, the hardness ranging from 2 to 2.5. The specific gravity is 4.73 to 4.86. Pyrolusite often occurs as reniform coatings associated with other manganese minerals. It is sometimes columnar and often granular massive. Pyrolusite frequently occurs as pseudomorphs after the characteristic radiating needles of manganite. It is usually a secondary mineral formed by the dehydration and oxidation of other manganese minerals. Due to its physical structure and chemical properties pyrolusite is the manganese oxide preferred by the dry-battery industry.

Psilomelane ($4\ MnO_2\ (Mn, Ba, K)\ O.nH_2O$)

Psilomelane is an oxide of variable composition containing 45 to 60 percent manganese and like pyrolusite usually contains several percent water. Many specimens contain a rather large percentage of barium; some of the samples examined had as much as 15 percent of barium oxide. It is a hard, black, opaque, amorphous mineral with a dull submetallic luster and conchoidal fracture, commonly found in massive, reniform, stalactitic, or botryoidal forms. Its hardness ranges from 5 to 6 and its specific gravity from 3.7 to 4.7. In concretionary masses common in many deposits, psilomelane displays a marked concentric structure due to alternation of hard and soft layers of the mineral. The varying hardness probably is due to variations in the water content of the psilomelane. When free from other manganese oxides psilomelane can be readily identified by its superior hardness and lack of crystallization.

Manganite ($Mn_2O_3.H_2O$)

Manganite, a hydrous manganese sesquioxide, contains 62.4 percent manganese and 10.3 percent water. It is a steel-gray to iron-black, opaque mineral of medium hardness (4.0) and a specific gravity of 4.2 to 4.4, commonly found in radiating needle forms or in feltlike masses of fine interlocking needles. It has a dark reddish brown streak and a submetallic luster.

Hausmannite (Mn_3O_4)

Hausmannite, an oxide of manganese, theoretically containing 72.1 percent manganese, is a black to brownish black opaque mineral, commonly crystalline, with a submetallic luster and a specific gravity of 4.73 to 4.86. It has a hardness of 5.0 to 5.5 and a brownish black streak. A fresh fracture usually shows numerous bright, shiny crystal faces.

Franklinite ((Fe, Zn, Mn) O.(Fe,Mn)$_2$O$_3$)

Franklinite is commonly found only in the deposits of Franklin Furnace, N. J. Its manganese content is variable, ranging from about 10 to 20 percent. It is an iron-black mineral with a metallic luster and reddish brown to black streak. Its specific gravity is 5.0 to 5.2, and its hardness 5.5 to 6.5. It is usually associated with zincite and willemite, and its structure is massive to granular.

Carbonate Minerals

The most common manganese carbonate mineral is rhodochrosite ($MnCO_3$). However, in addition to this mineral there is a series of isomorphous calcium and manganese carbonates with compositions ranging from that of calcite to that of rhodochrosite. Minerals in this series are termed manganocalcites and are not uncommon. Kreiger (215) found that as the mineral grades from calcite to rhodochrosite the indices of refraction and specific gravity increase gradually. He also showed that variation of the isomorphous constituents could be detected by X-ray diffraction study. In addition to the calcite-rhodochrosite series of manganese carbonates a more complex series is found in the ores of the Chamberlain (S. Dak.) district. These ore minerals probably consist of an isomorphous mixture of calcite, magnesite, siderite, and rhodochrosite.

Rhodochrosite ($MnCO_3$)

The manganese carbonate, rhodochrosite, contains 47.8 percent manganese when pure. It is usually light rose, although other shades are not uncommon. Rhodochrosite is a translucent mineral with a vitreous luster and a colorless streak. Its specific gravity is 3.45 to 3.6 and its hardness 3.5 to 4.0. Rhodochrosite often occurs in cleavable massive form with a distinct rhombohedral cleavage. It frequently occurs with rhodonite, from which it usually can be distinguished by the softness of rhodochrosite and by the reaction of rhodochrosite with warm hydrochloric acid. Chemical analyses or specific-gravity determinations are sometimes necessary to distinguish rhodochrosite from the manganosilicates.

Silicate Minerals

The manganese silicates have no importance as ores of manganese but are of interest due to their association with the oxides. Rhodonite and braunite are the two most common silicates. The hydrous silicate, bementite, is found

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in large quantities in the manganese deposits of the Olympic Peninsula, Wash., where it sometimes is the major constituent of the ore body. Occasionally neotocite, a rather rare mineral of similar composition, is found with the bementite in the Washington deposits.

Rhodonite ($MnSiO_3$)

Rhodonite, the metasilicate of manganese, theoretically contains 41.9 percent manganese and 45.99 percent silica. It is usually deep rose and translucent, with a vitreous luster and a colorless streak. The fracture of rhodonite is conchoidal to uneven. Its specific gravity is 3.4 to 3.7, and its hardness (5.5 to 6.5) is sufficient to distinguish it from rhodochrosite, with which it is sometimes confused. Its structure is commonly massive, cleavable to compact, or in embedded grains.

Braunite ($3\ Mn_2O_3.nMnSiO_2$)

The silica content of braunite is variable, and according to Schneiderhohn and Ramdohr (341) the silicate molecule may sometimes be absent. Most varieties contain about 60 percent manganese and about 9 percent silica. Braunite is a black to steel-gray opaque mineral with a submetallic luster and a brownish black streak. Its specific gravity ranges from 4.72 to 4.82 and its hardness from 6.0 to 6.5. It commonly occurs in granular form with euhedral tetragonal crystals. The crystallizing tendency of braunite is so well pronounced that it usually serves as a method of identification.

Bementite ($8\ MnO.\ 5\ H_2O\ .\ 7\ SiO_2$)

Bementite is a hydrous manganese silicate of somewhat uncertain composition, containing usually about 31 percent manganese and 35 percent silica. The mineral from the Olympic Peninsula district is light gray to grayish brown and has a vitreous luster, a splintery fracture, a hardness of about 6.0, and a specific gravity of about 3.1. It is transparent in splinters but upon weathering becomes opaque. Microscopic examination shows that the mineral usually consists of a fine-grained felted aggregate of fibers and plates.

Sulphide Minerals

Two manganese sulphide minerals are known - alabandite (MnS) and hauerite (MnS_2). They have no commercial importance as a source of manganese and are of interest only from a scientific viewpoint. Alabandite is the more common mineral and has been reported by Hewett and Rove (161) as occurring in a number of western localities. Hauerite is a rare mineral.

Alabandite (MnS)

Alabandite theoretically contains 63.1 percent manganese. It is an iron-black to brown mineral with a submetallic luster and an olive-green streak, which is quite distinctive and often serves as a means of identification. Alabandite has a specific gravity of 3.95 and a hardness of 3.5 to 4. It is usually granular massive in structure, with perfect cubic cleavage.

Mineragraphic Identification of Opaque Manganese Minerals

Identification of the various oxide minerals is frequently difficult. Their intimate association and the alteration of one mineral to another are confusing. Pseudomorphs are abundant and misleading. Sometimes positive identification is possible only by study of polished sections under the microscope, accompanied by microchemical tests. Microscopic methods of identification of some of the more important opaque manganese minerals have been given by Thiel (367,368), Short (348) and Fairbanks (89) and by Cooke and associates (58).

The authors have used polarized light in conjunction with the metallographic microscope in the differentiation of the opaque manganese minerals and have found it of primary importance. An examination by this method makes it possible to place them immediately in one of two classes, anisotropic or isotropic.

Anisotropic Minerals.

Three of the more common opaque manganese minerals -- pyrolusite, manganite, and hausmannite -- are strongly anisotropic, each giving four extinctions per revolution. (Most anisotropic minerals give only two extinctions.) If these three minerals occur in particles of sufficient size a hardness test suffices to identify them. Pyrolusite is soft (2 to 2.5), manganite is of medium hardness (4.0), and hausmannite is hard (5 to 5.6). In fine-grained aggregates pyrolusite and manganite are not identifiable by hardness tests, and recourse must be had to an etching treatment. A short etch with an 8 percent solution of sulphurous acid rapidly darkens and pits pyrolusite, while manganite is virtually unaffected. Photomicrographs of unetched and etched sections of pyrolusite and manganite are shown in figure 2, A and B. Hausmannite may be differentiated from pyrolusite and manganite by its hardness, by the excellent polish it takes, and by a characteristic reticulate etch pattern with a saturated solution of stannous chloride. Figure 3, A, shows the usual crystalline structure of hausmannite and the strong aniactropism of the mineral.

Isotropic Minerals.

Four of the more common opaque minerals are isotropic -- psilomelane, braunite, franklinite, and alabandite. Psilomelane is amorphous and when etched with sulphurous acid darkens, giving a sorbitic structure. Banded structures are rather common. Psilomelane of several generations is often present in the same specimen. Figure 4, A, shows a specimen of psilomelane unetched, the secondary psilomelane being much clearer than the older variety. Figure 4, B, shows the large amount of quartz in the primary psilomelane and the sorbitic pattern brought out by etching. Braunite usually can be identified by its tendency to form euhedral crystals and by the fact that it is not etched by sulphurous acid and but slightly by stannous chloride. The twinning sometimes shown by braunite is brought out in figure 3, B. Franklinite occurs commonly only in the mines at Franklin Furnace, N. J. A blowpipe test on charcoal for zinc is the surest means of differentiating it from the other manganese minerals. Alabandite can be readily identified by its olive-green streak and

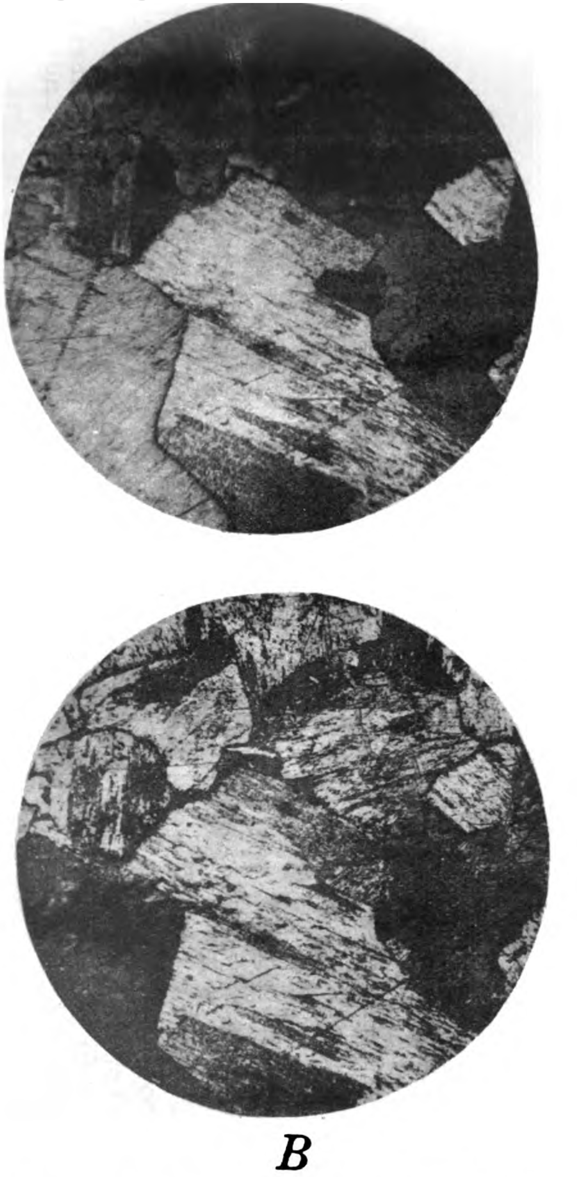

Figure 2.- Pyrolusite and manganite. Little Florida Mountains, N. Mex. Dark areas pyrolusite, light areas manganite. (75 x). A, Unetched. B, Etched 5 seconds with 8 percent solution of sulphurous acid.

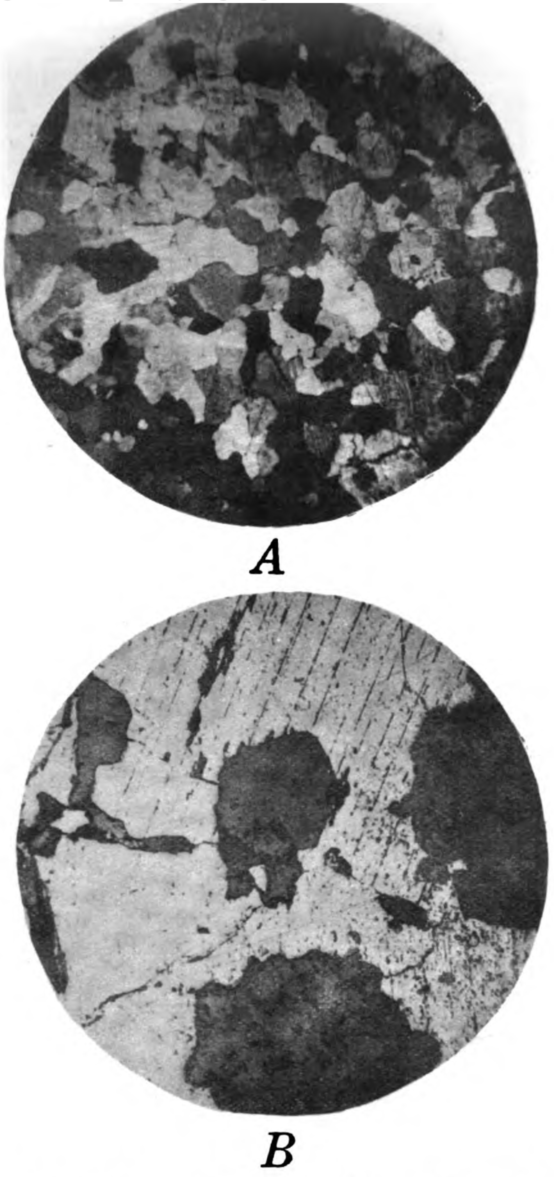

Figure 3.- A, Hausmannite. Cushman, Ark. Polarized light. Unetched, 70 x. B, Braunite. Light area braunite; dark area gangue. Note twinning in braunite. Unetched, 75 x.

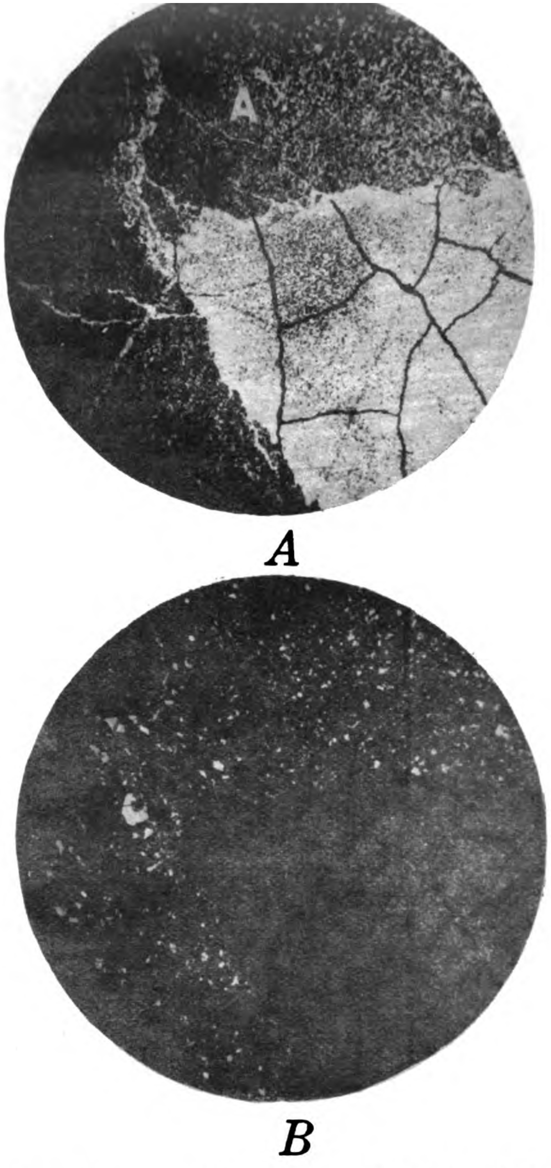

Figure 4.- Psilomelane. Crimora mine, Virginia. Bright areas are quartz. (70 x). A, Unetched: (1) Impure psilomelane; (2) secondary. B, Etched with 8 percent sulphurous acid for 80 seconds.

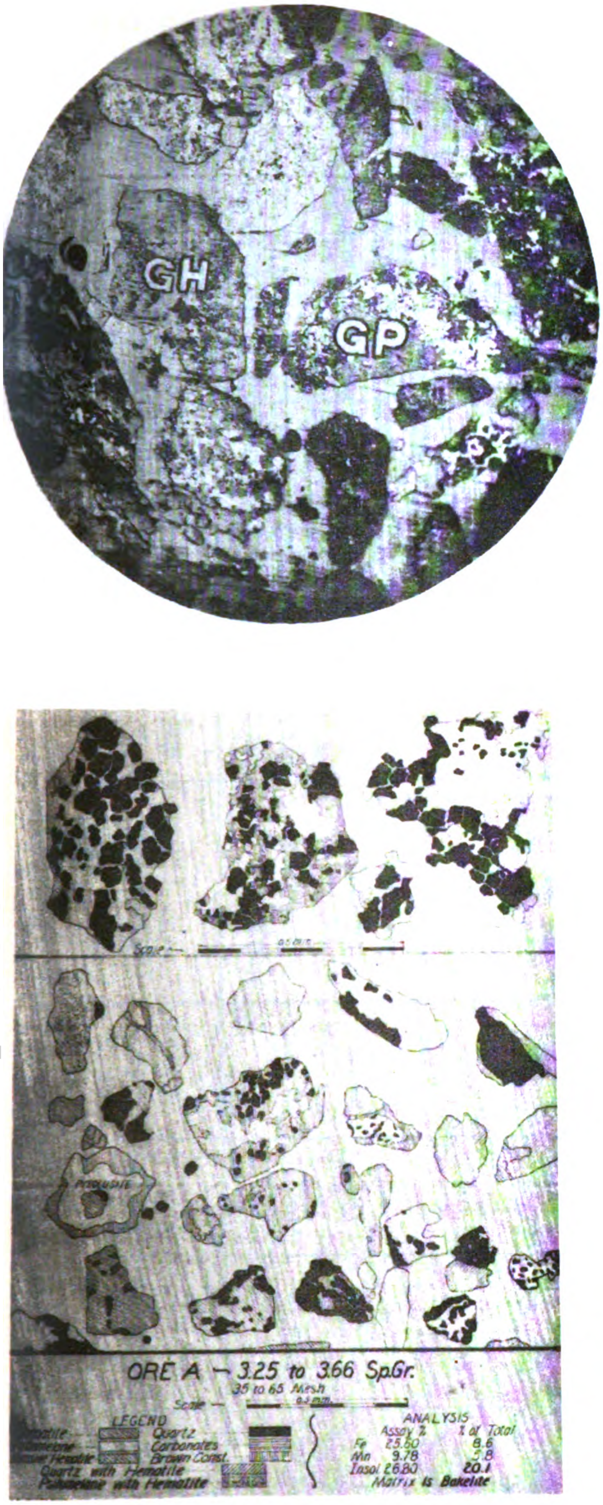

Figure 5.- Briquetted Cuyuna ore. A, Polished section; 35- to 65-mesh portion, float-and-sink fraction 3.25 to 3.66 sp. gr. Illustrates intimate interlocking of siliceous gangue (G), hematite (H), and psilomelane (P). 50 x. B, Camera lucida drawing of selected particles.

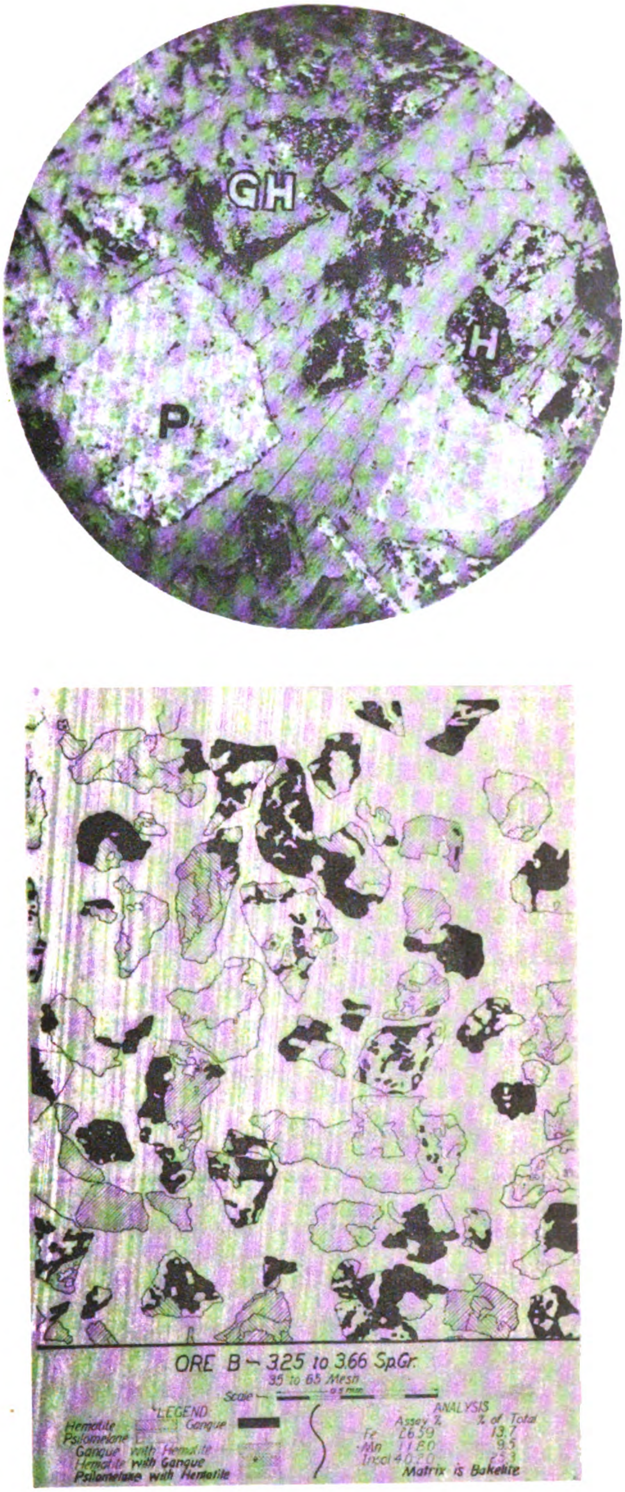

Figure 6.- Briquetted Cuyuna ore.. A, Polished section; 35- to 65-mesh portion, float-and-sink fraction 3.25 to 3.66 sp. gr. Gangue (G), hematite (H), psilomelane (P). 50 x. B, Camera lucida drawing of selected particles.

TABLE 6. - Mineragraphic Characteristics of More Common Opaque Manganese Minerals

Mineral	Examination in polarized light	Hardness	Color	Color of Powder	Structure	Reaction to etching solution		
						8 percent solution of H_2SO_3	Commercial H_2O_2	Saturated sol. $SnCl_2$
Psilomelane......	Isotropic	5 to 6	Gray.	Black.	Nodular amorphous.	Darkens with sorbitic pattern.	Effervesces vigorously with etching.	Tarnishes with etching.
Braunite..	do.	6 to 6.5	do.	Brownish black.	Commonly granular with tetragonal crystal outlines.	No reaction.	Slowly effervesces without staining.	Etches slightly to grayish brown.
Alabandite	do.	3.5 to 4	Sphalerite gray.	Olive green.	Usually granular massive, perfect cubic cleavage.	Etches rapidly; stains white; H_2S liberated.	No reaction.	Fumes tarnish; H_2S liberated.
Pyrolusite	Anisotropic.	2 to 2.5	Gray, almost white.	Black.	Radiating columnar and granular massive; frequently pseudomorphic after manganite.	Darkens rapidly; deeply etched.	Effervesces vigorously.	Deep etch; pitted.
Manganite.	do.	4	Gray.	Brownish black.	Usually in radiating crystals.	Darkens slightly with long etch.	Slowly effervesces without staining.	Short contact brings out crystal structure.
Hausmannite	do.	5 to 5.6	Bluish white.	Dark reddish brown.	Generally crystalline.	No reaction.	do.	Tarnishes brown; rubs to reticulate etch pattern.

by the liberation of hydrogen sulphide when etched with stannous chloride. Table 6 shows the differentiation of the more common opaque manganese minerals. For the transparent minerals ordinary petrographic methods are used.

Impurities Associated with Manganese Minerals

Manganese ores, like those of other metals, contain impurities which must be removed by ore-dressing or metallurgical processes. Some impurities are present as discrete particles, which can usually be rejected by ore-dressing methods unless too finely intermixed. Chemically combined or dissolved impurities can be eliminated only by metallurgical processes.

Some ores containing manganese are mined in the West for a flux in nonferrous metallurgy. Frequently they contain, besides manganese, some lead, zinc, silver, gold, and other metals. Because no manganese is recovered from concentration of these ores they will not be discussed.

The impurities commonly found in ores of manganese may be classified into four general groups, namely:

(1) Metallic--iron, zinc, lead, copper and silver; (2) gangue--silica, alumina, lime, magnesia, and baryta; (3) volatile--water, carbon dioxide, and organic matter; and (4) miscellaneous--phosphorus and sulphur.

Of the metallic impurities, iron is by far the most common. The iron occurs in oxide form, which is usually difficult to remove by ore-dressing methods; magnetic separation may be possible after a reducing roast. Gravity concentration sometimes makes a concentrate enriched in manganese and impoverished in iron. The amount of iron present in a final product determines the type of alloy that can be made. Usually products with more than 1 part of iron to 9 parts of manganese cannot be used for the manufacture of ferromanganese. The other metallics, such as zinc, lead, copper, and silver, in ores utilized for their manganese are found in merchantable quantities in the Butte carbonate deposits. With the exception of silver, these elements are present as sulphides, and although they occur in rather small quantities they should be removed by ore-dressing methods. The chief reasons for removal are that sulphur and zinc are objectionable in the metallurgical processes for the production of ferro-alloys and that economic losses result because none of the metals are recoverable in these processes.

Gangue, such as silica, alumina, lime, magnesia, and baryta, is found in ores of manganese. These impurities, which comprise the slag-forming constituents of the ore, must be kept within allowable limits if the metallurgical treatment be economic. They pass largely into the slag when smelted, and although a certain amount of slag is essential for the removal of injurious impurities, such as sulphur, a large amount of gangue with the consequent production of large slag volumes is highly undesirable. Large amounts of gangue require large amounts of coke. Much slag is formed, and as the slag always contains manganese, the amount of metal recoverable, other conditions being equal, is inversely proportional to the amount of slag formed.

The gangue constituents frequently are classed as acid or basic, according to their bahavior in the furnace. Of the more common impurities silica and alumina are usually considered as acid, although the action of alumina is somewhat uncertain. Lime, magnesia, and baryta are considered as basic. Manganese-alloy furnaces are run to produce basic slags and for this reason basic impurities are less objectionable than acid impurities. Silica is by far the most common of all the gangue and is found in nearly all ores. The elimination of silica is usually the chief problem confronting the ore-dressing engineer. Alumina in the form of clay is a troublesome impurity in many ores. When it occurs with hard or nodular manganese minerals its elimination is usually easy, but when the manganese minerals are soft and friable removal is difficult. The basic impurities lime, magnesia, and baryta are seldom found in troublesome quantities. However, in some districts where the manganese mineral is predominately psilomelane, undesirable amounts of baryta may be present. In such instances the barium content of the ore cannot be lowered by ore-dressing methods. In the Chamberlain (S. Dak.) district lime and magnesia are present as carbonates in an isomorphous mixture with rhodochrosite and siderite. Their elimination by ore-dressing methods does not seem probable. With the exception of the Chamberlain ore, or ores of psilomelane with high barium content, the basic impurities in the ores studied have been present in small quantities or can be easily rejected.

Water and carbon dioxide are the two important volatile impurities. Water is present to some degree in virtually all ores. It is not simply a diluent but also lowers the metallurgical efficiency of the blast furnace. The removal of water is frequently desirable. Some wad ores of Arkansas contain as much as 30 percent of water, and since these ores are usually marketed in the Birmingham district the fallacy of paying freight on so much water across several States can be readily seen. Carbon dioxide is important only in rhodochrosite ores. According to some blast-furnace operators carbon dioxide is harmful to the operation of a furnace, as it interferes with the usual carbon monoxide: carbon dioxide ratio. Whether or not this difficulty exists it is important that rhodochrosite ores be calcined before shipment, as the manganese content can be increased materially and freight charges saved by elimination of the carbon dioxide, which in pure rhodochrosite amounts to 38.3 percent.

Sulphur and phosphorus are objectionable impurities in any manganese ore. Upon smelting, the phosphorus content of the ore passes almost entirely into the ferro-alloys. Since low-phosphorus alloys are required, a high-phosphorus ore cannot be used for making ferromanganese or speigeleisen. Phosphorus is usually chemically combined or so intimately associated with the manganese and iron that its elimination by ore-dressing methods is impossible.

In smelting operations sulphur usually passes into the slag, hence its effects are not as harmful as those of phosphorus. Sulphur was not found to any extent in domestic ores, except in the Butte carbonate ores, where it occurs as sulphides. The sulphides usually can be eliminated by ore-dressing processes.

ORE DRESSING OF ORES OF MANGANESE

Ore dressing is the art of physical separation of ore from gangue. The segregated ore is "concentrate" and the gangue is "tailing". To effect a separation of ore and gangue various physical properties of the minerals are utilized. The use of these physical properties to segregate discrete mineral grains differentiates ore dressing from metallurgy, which deals with chemical reactions. In metallurgy some natural compounds are destroyed for new ones more favorable to the separation sought. Ore dressing permits removal of some of the gangue before metallurgy begins; thus, it is a link between the mine and the metallurgical plant.

Ore dressing hypothecates the liberation of discrete economic mineral grains; the gangue mineral grains need not be liberated from each other. The first step in liberation is incident to the mining, as a result of blasting. After that breaking, crushing, and grinding follow until liberation is obtained.

The more important physical properties employed in dressing ores of manganese are color, luster, hardness, magnetic permeability, specific gravity, and surface phenomena.

Color and Luster

Hand-sorting or picking may be employed when the minerals are liberated from each other, and the color and luster permit identification. Sometimes the mineral is removed by hand, sometimes the waste is removed, and sometimes each is thrown into its respective bin. The mineral pieces removed are 2 inches to 2 feet in size. The required labor is cheap, and the skill in close differentiation by trained men and women sorters puts to shame the best college mineralogists. One advantage of hand-sorting is the removal of rope, wood, steel, and dynamite incident to mining.

Hardness

With respect to the oxide ores of manganese, with the possible exception of pyrolusite, a rule about hardness may be laid down, namely, that the coarsest sizes (the hardest) resulting from crushing have the highest manganese content. Sometimes screening on a single screen of the correct size will make concentrate and tailing. At any rate, the hardness characteristic favors gravity concentration, which requires material that is not too fine. This hardness characteristic warrants further comment. Not only are the coarser sizes of higher manganese content than the finer sizes, but also the coarse manganese-bearing grains are richer than the fine manganese grains. To state this relationship in another way: The hardness increases with the purity. This is not true of rhodochrosite, which occurs in a high state of purity and has clean mineral in all sizes. On crushing rhodocrosite fine enough to liberate adhering gangue all sizes contain clean mineral.

Magnetic Permeability

Probably no other ores are so generally permeable to magnetic forces as the ores of manganese. The magnetic permeability of manganese minerals in many instances is due to the presence of iron. Manganese minerals of the highest purity can however be concentrated by the use of high-intensity separators, and the manganese compounds themselves may under certain conditions be ferromagnetic. Rhodochrosite is so susceptible that the commercial use of magnetic separators has been considered. The magnetic separation of an oxide ore, largely pyrolusite, is in commercial practice. High-intensity magnetic separators are required for separation of the manganese minerals. However, the permeability of these minerals is frequently higher than that of the associated iron minerals. Such oxides as pyrolusite and psilomelane have been separated from the less-permeable limonite. Martin (243) states that precipitated manganese dioxide is quite magnetic. The iron content was only 0.096 percent.

The use of the magnetic properties of the manganese minerals as a means of making commercial separations has not been adopted more widely because of the cost of the equipment and the necessity for preliminary drying and sizing of the ore.

Specific Gravity

When the ratio of weights (in water) of unit volumes of gangue and mineral is 1 : 1-1/2 or greater gravity concentration must be considered.

The outstanding methods of gravity concentration are jigging and tabling; the first is by vertical currents of water and the second by horizontal currents. Since these methods, with all the supplementary devices and procedures, are described in the many textbooks on ore dressing and in technical publications the discussion will be abridged.

Jigs and jigging permit many classifications. Only two will be mentioned; the first relates to one of the mechanical features, and the second depends on preparation of the feed. The first is subject to two divisions; the sieve may be movable or it may be fixed.

(1) When it is movable the jig may be called a basket jig because the sieve constitutes the bottom of a frame or basket. The basket works in a tank of standing water and hence is most desirable when water is scarce. The simplest pattern is worked by hand and is called a hand jig. The feed and discharge are intermittent. Its simplicity and low cost make the hand jig a desirable concentrator where a small mine is being developed. Larger basket jigs are driven by power; and some of them, in addition to the up and down motion of the basket, impart a horizontal throwing action which speeds up the travel of the charge. They are at their best in handling coarse material.

(2) Fixed-sieve jigs are more common and are usually home-made. The motion of the water is actuated by a plunger, either at the side of the jig cell or under it. Fresh water must be added to replace what passes over the tailboard and through the hutch. Since it is always added to the plunger the amount affects the rate of suction. When much water is used fine material rides on the charge; when little water is added a suction is created that draws

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fines into the hutch. A jigman prides himself on the adjustment of suction to suit the particular ore. Manganese ores, usually lean in the fines, would require minimum suction--that is, maximum amount of water to throw the fines into the tailings.

The other classification--that depending on preparation of the feed--is no less important than the first. The feed may be sized or mixed (unsized).

The sized feed is the only kind that is metallurgically correct. When the ore is difficult--that is, when the mineral is only moderately heavier than the gangue--the feed should be sized between limiting screens with openings that have a ratio not greater than 1 : 1 1/2. To do otherwise is to violate natural laws for expediency. When the mineral is heavy, like galena for example, and liberated from the gangue almost any procedure will recover it, but if it is disseminated through the gangue so that the composite grains have an intermediate density thought must be given to precision. The jigging of manganese ores is most satisfactory when the feed is sized. The best method to draw concentrates is through correctly spaced holes in the sieve.

Table concentration is for material finer than 3 mm. Just as a jig feed requires sizing, so does a table feed require classification with a multiple-spigot hydraulic classifier. The more difficult ores need to be classified more closely than the easy ones. Since the fine sizes of manganese oxides have the low-grade and lightweight grains segregated therein close attention should be given to table concentration.

Before resorting to jigging and tabling the ore should be fractioned on heavy liquids. If heavy liquids do not yield concentrates that are up to grade it is folly to try to make machinery do it. Some manganese oxides are too inherently foul to yield concentrates by any kind of physical separation. Many examples of float-and-sink tests are given in this report.

Surface Phenomena

The practice of flotation began in Australia about 1904 and was taken up with vigor in the United States about 10 years later. It depends on phenomena exhibited at the mineral-water interface. When the ore is crushed fine enough these phenomena predominate over those due to mass, so that minerals with different surface properties may be separated by flotation. Flotation is fundamentally gravity concentration because it depends on the attachment of air bubbles to the mineral grains to make a composite aggregate lighter than water; thus the mineral is brought to the surface of the pulp and removed.

Only during the last decade has flotation of minerals other than sulphides, native metals, and a few of the oxidized copper and lead minerals become important. Many nonsulphide (53) minerals are now known to be floatable, and the number that can be separated by flotation is growing rapidly.

Flotation as a process for the treatment of ores of manganese was investigated, and many ores were found to be amenable to it. Of the manganese minerals, rhodochrosite is readily floatable. The oxide minerals, such as pyrolusite, manganite, and psilomelane, are less floatable, but in many instances satisfactory separation of these minerals is possible. The process works best when the manganese minerals are clean, and the gangue is hard and noncalcareous. The reagents used in the flotation of manganese ores are similar to those used in other nonsulphide separations, namely, soap or a fatty acid as a collector, pine oil or cresylic acid as a frother, sodium silicate as a dispersing agent, and sodium carbonate to control the alkalinity. The flotation of manganese ores other than rhodochrosite has not been demonstrated successfully in large-scale mill operation.

Much literature on flotation is available, and what follows in this report will show some preliminary work on the flotation of ores of manganese.

EXPERIMENTAL STUDY OF ORE DRESSING OF ORES OF MANGANESE FROM VARIOUS DISTRICTS

Scope of Work

The following pages will be devoted to brief descriptions of some of the various manganese districts and to a resume of experimental work at the United States Bureau of Mines Mississippi Valley Experiment Station, Rolla, Mo. The order of treatment is alphabetical by States.

Heavy liquids were used to determine the amenability of the ore to gravity concentration. The rapidity with which tests can be made with heavy liquids made possible the examination of a great many samples. The results of the float-and-sink tests indicate the theoretical grade of concentrates and the recovery of mineral that can be expected from commercial equipment when working on the same size of ore. As a general rule, it may be said that jigs and tables will not give as high a recovery as float-and-sink tests indicated, but this is frequently compensated by a somewhat higher grade concentrate due to the loss of some of the middling grains in the tailing. The use and care of heavy liquids have been reported in other publications (52, 283, 365).

The authors are not in a position to estimate the amount of ore in the various districts, and no attempt will be made to give probable treatment costs of these ores by different processes. The purpose of the investigation was to determine what could be done toward concentrating the manganese ores of the country by ore-dressing methods. This aim has been kept in mind, and the determination of what could be done has been given more thought than the question as to whether such processes would be profitable at present.

Kingman District, Ariz.

Location and Extent

Large amounts of low-grade ores have been reported in recent years as occurring in the district north of the Williams River in Mohave County, Ariz., between Kingman and Wickenberg and known as the Kingman district. These deposits have been described by Jones and Ransome (182) and also by Wilson and Butler (393).

Mineralogy

The manganese in high-grade ore is in the form of psilomelane and pyrolusite, replacing limestone. The manganese minerals are in slaggy vesicular aggregates. The only gangue minerals noted are gypsum, clay, and a small amount of chalcedony.

The samples of low-grade ores examined contained quartz and feldspar grains with some clay. Manganese oxides are scattered in finely divided form throughout.

Concentration Tests

High-Grade Ore. - The sample studied analyzed 38.3 percent manganese, 1.6 percent iron, 16.7 percent insoluble[7], and 0.025 percent phosphorus.

A slight enrichment can be accomplished by crushing and washing out the slime, which is mostly clay. Float-and-sink tests of ore sized between 1/2 inch and 14 mesh showed no liberation of gangue. Similar tests of ore sized between 14 and 65 mesh showed that the percentage of insoluble[7] would be reduced from 17.7 to about 15.2 percent if tabling were practiced. Further crushing would undoubtedly favor production of somewhat higher-grade concentrates. The high-grade ores of this district, while limited in amount and quite siliceous, have the desirable characteristics of possessing a low iron and phosphorus content.

Low-Grade Ores. - Three samples of low-grade ores, said to be representative of large deposits, were examined. The samples looked much alike and consisted of brownish black porous material, the particles of which could be readily broken with the fingers. Many pieces glistened, due to the presence of small quantities of calcite. The major part of the material is quartz, feldspar, and clay. Manganese oxides are scattered in finely divided form throughout. Analyses of the samples examined follow:

Sample	Assay, percent				
	Mn	Fe	Insol.	P	CaO
1	8.1	2.3	68.6	0.057	1.69
2	5.7	2.8	72.4	.059	---
3	5.9	2.4	63.6	.059	---

As all three samples had quite similar characteristics, that of highest grade was chosen for experimental work. When the sample was crushed to one-half inch it gave a slight enrichment of the coarser sizes, due to the tendency of the clayey portion to slime.

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[7] To simplify the chemical work many samples listed are reported in terms of insoluble rather than as silica. On most ores the values for insoluble and silica are very close. Insolubles are obtained by dissolving in aqua regia and taking to dryness. The residue is then treated with concentrated hydrochloric acid, diluted with water, and filtered. The insoluble residue and filter paper are ignited and weighed and reported as insoluble. True silica may be determined from the insoluble, if desired, by the usual methods.

Float-and-sink tests of sized portions were made in a liquid with a specific gravity of 2.90 and showed conclusively that high-grade concentrates could not be made by jigging or tabling. The cleanest concentrate contained only 25 percent of manganese and had 38 percent of insoluble. The recoveries of manganese in gravity concentrates would be poor.

There were attempts to concentrate by flotation, but the results were unsatisfactory. Concentrates were made, but their silica content was always high. Intimate association of the mineral with the gangue, large quantities of soluble salts in the ore, and the presence of much clay contributed to the failure of this process.

From the experimental work on the low-grade ore its concentration by present ore-dressing methods appears hopeless. Claims have been made that the ore is amenable to leaching processes. If a low-cost process can be used the deposits may prove valuable. Undoubtedly some higher-grade portions of the ore deposits can be used for metallurgical purposes.

Batesville District, Ark.

Location and Extent

The Batesville district, near the town of the same name in northern Arkansas, has long produced manganese ore and ferruginous manganese ores. This district is an east-west belt 4 to 8 miles in width and about 24 miles in length. The area has particular interest due to the widespread occurrence of manganese minerals and to the variety of the types of deposits in which they occur.

Types of Deposits

Several excellent geological reports are available, the most recent being by Miser (260). The deposits may be grouped in the order of commercial importance as follows:

1. Residual deposits derived from the Fernvale limestone.
2. Deposits in the Cason shale and its residual clay.
3. Replacement deposits in the Fernvale limestone.
4. Replacement deposits in clay.
5. Transported deposits in stream gravels.

A small production has come from the last two types of deposits, but as they have interest only from a scientific viewpoint rather than as a source of supply of manganese they will not be discussed.

Residual Deposits Derived from Fernvale Limestone. - Ore deposits of this type are the most important in the district. They have yielded the greater part of the high-grade ore as well as a considerable proportion of the low-grade ore. The ore occurs disseminated in the residual clay in all gradations of form from large lumps of hard ore to irregular bodies of wad ores. The chief manganese minerals are psilomelane, hausmannite, wad, and braunite. The latter is the least common. The subject will be discussed under lump ores, manganese-bearing clays, and wad ores.

Lump ore. - The lump ore is of high grade and can be recovered readily from the clay and particles of chert. Some analyses of lump ores mined during 1929 showed that they contain 46.0 to 58.0 percent of manganese and less than 5 percent of silica. These hard ores are also characterized by their low phosphorus content compared with the softer wad ores.

The coarser ores are generally hand-picked, but where the ore occurs in finer form log washing, followed in some instances by jigging, has been found satisfactory. The problem of working these deposits has been largely one of mining. The manganese mineral is irregularly distributed through the clay in pockets surrounded by clay containing little or no ore. Numerous attempts to open mines on a large scale and to employ steam shovels have failed due to the spotty character of the ore deposits, to the large amount of valueless gangue that must be handled, and to the occurrence of limestone pinnacles. Production now comes from a number of small operations where the principal equipment is still wheelbarrows, picks, and shovels.

Manganese-bearing clays. - The recovery of the small particles of manganese minerals associated with clay in the residual deposits is difficult. The amount of manganese occurring in finely disseminated form in the clay is large, and a mill was erected on Polk Bayou by Miller & Rinehart in 1926 to treat this type of material. This operation represented the first definite effort in the district to recover such material.

Methods at this mine were described by Furness (104, pp. 179-180) as follows:

> ".....The property is equipped with an experimental mill, which consists of two 35-foot log washers, Oliver classifier, Wilfley tables, and a 35-foot rotary drier. The method of mining the ore consists of a partial stripping with a steam shovel, followed by pick, shovel, and wheelbarrow work. The surface of the bedrock limestone on which the residual clays are found is very irregular with extensive solution channels and potholes among residual pinnacles of limestone. The clay containing manganese is trammed to the mill and delivered to the log washers. There is no overflow from the log washers; they are used solely as agitators. The discharge from the log washers, including the wash-water sand and ore, is passed over a fine screen; the undersize from the screen is flushed to Dorr grade C classifiers. The product from these classifiers is treated on Wilfley tables. The oversize from the first screening is crushed by rolls to 10 mesh and then concentrated on the Wilfley tables. The concentrates are passed through the rotary drier where the moisture is reduced to less than 7 percent. The capacity of the mill is about 100 cubic yards per 12 hours, and the recovery is 20 tons of concentrate of approximately the following analysis: Mn, 20 to 25 percent; Fe, 18 to 20 percent; SiO_2, 14 percent; Al_2O_3, 12 percent. The rejects and tailings from the tables,

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containing from 16 to 18 percent of manganese, are impounded in a tailing pond. The crude ore contains about 12 percent of manganese. The product of the mill is being purchased by the Tennessee Coal, Iron & Railroad Co. at 42 cents a unit. Miller & Rinehart control more than 1,000 acres of land on Skunk Creek, and they claim that the results of drilling and test stripping indicate several million tons of concentrating ore."

The operation of this mill was not satisfactory due to the high insoluble and phosphorus content of the concentrate and the large losses of manganese in the tailings. A sample of the sinter produced from the concentrates had the following analysis: manganese, 17.4 percent; iron, 19.2 percent; insoluble, 20.8 percent; and phosphorus, 1.443 percent.

Concentration tests. - Samples of the manganiferous clay at the Miller-Rinehart property were taken in 1929 and studied to determine the character of the ore and the possibility of making higher-grade concentrates than had been produced. The samples had a tenor of only 6.6 percent manganese, a figure somewhat lower than the reported feed to the mill. Nevertheless, the samples are believed to be fairly indicative of the grade of remaining ore. The ore consists of fine particles of hard manganese oxides and of soft amorphous particles scattered through a rather stiff chocolate clay. A small amount of chert particles is also present. Table 7 gives a screen analysis of the manganese-bearing clay and shows the extreme fineness of the material. Approximately 55 percent is finer than 200-mesh; and this fine material, although lower in manganese than the coarser sizes, contains about 40 percent of the total manganese.

TABLE 7. - Screen Analysis of Manganese-Bearing Clay

Size, mesh	Weight, percent	Assay, percent				Percent of total		
		Mn	Fe	Insol.	P	Mn	Fe	Insol.
Plus 48.....	18.8	10.0	21.6	18.9	---	30.5	34.1	8.3
48 to 100...	9.4	8.0	15.2	33.5	---	12.1	12.0	7.3
100 to 200..	16.6	6.4	11.1	42.5	---	17.2	15.4	16.4
Minus 200...	55.2	4.5	8.3	53.0	---	40.2	38.5	68.0
Composite.	100.0	6.2	11.9	43.0	1.04	100.0	100.0	100.0

An attempt was made to concentrate this ore by screening out the material coarser than 100-mesh and tabling it, but the tabling was not commercially successful. Hydraulic classification as undertaken by the operators was tried, but in no instance could a satisfactory separation be made.

Due to the large percentage of the manganese in the form of extremely fine particles gravity concentration does not appear promising. The flotation process also offers very little hope, as the clay which forms the bulk of the material absorbs large quantities of reagents, tends to come up in the froth, and gives a siliceous concentrate.

Wad ore. - A considerable amount of ferruginous manganese ore has been mined in the past and is now being produced in the district. The large lumps of high-grade ore are generally picked from these ores and shipped separately. The greater part of the material can best be described as wad ore and is characterized by a lower manganese and higher iron, phosphorus, and insoluble content than the lump ores. The material is also quite soft and porous and usually has a moisture content of approximately 30 percent.

An average analysis of a shipment of 1250 tons of wad ore,during 1928 is as follows: Manganese, 25.4 percent; iron, 16.4 percent; silica, 15.5 percent; alumina, 9.44 percent; and phosphorus, 1.18 percent. The moisture content was 29 percent.

Due to the readiness with which the wad ores disintegrate gravity concentration has questionable value. The silica content could undoubtedly be reduced somewhat, but a large portion of the manganese would be lost in the slime. The high moisture content of the wad ores costs the producers an appreciable sum each year in added freight charges. The erection of a small custom-sintering plant in the district would seem justified. The use of nothing more than a drying plant would have no value, as removal of the moisture would render the ore so dusty that it would be difficult to handle, and the dust losses would be great.

Deposits in Cason Shale and Its Residual Clay. - The following description of the deposits in the Cason shale is taken from Miser (260, pp. 57-58), who states:

> Manganese and ferruginous manganese ores are widely distributed in the Cason shale. The deposits have been worked at a number of places and have yielded most of the ferruginous manganese ores and a considerable part of the manganese ores that have been produced in the Batesville district. The Cason shale is generally present in the vicinity of Cushman and farther west. East of Cushman it is absent at most places, but the ore deposits in that area are larger and contain a higher manganese content and a lower iron content than the deposits farther west. The shale is thin, at no place exceeding 12½ feet in thickness, but its residual clay is 20 feet or more thick at the Montgomery mine, suggesting that the shale at that locality was probably more than 12½ feet thick.
>
> The ores consist of iron and manganese oxides, which are in places more or less intimately mixed. The manganese oxides are mainly psilomelane and the iron oxides include both red and brown oxides. These minerals occur as irregular masses, as thin horizontal seams and beds, and as "buttons", which are flattened concretion-like masses about an inch in their longest diameter.

A pilot mill was constructed in 1927 by M. R. W. Mining Co. of Memphis to concentrate the "button" ore of the Cason mine. The flow sheet of the mill was very similar to that of a mill in the tri-State lead and zinc district, and consisting of crushers, rolls, rougher jigs, cleaner jigs, and tables. The capacity of the mill was rated at 40 tons of crude ore per shift. Reports (85) state that during the time the mill operated 15 tons of concentrates, assaying 37 to 40 percent manganese, were recovered from each 100 tons of feed. The mill was operated only a short time and was not a success.

Analyses of the shale and the "buttons" are taken from tables by Miser (260, pp. 139-140) and given in table 8. The percentage of manganese in the "buttons" varies greatly, ranging from 5.85 percent in the red "buttons" to 50.41 in the black. The percentage of manganese in the greenish-gray shale in which the "buttons" occurred was 5.87 percent.

TABLE 8. - Analyses of Shale and "Buttons" from Cason Mine

Material	Assay, percent					
	Mn	Fe	SiO_2	Al_2O_3	CaO	P
Greenish-gray shale..	5.87	4.98	32.73	8.22	14.22	---
Red "buttons"........	5.85	3.08	2.73	5.68	29.85	---
Black "buttons"......	50.41	7.56	12.67	1.27	2.09	0.06

The Cason mine was inspected in March 1929. The mine was not in operation, and it appeared that much of the ore containing the relatively high-manganese black "buttons" had been removed. The shale exposed in the opencuts was largely greenish gray, and the "buttons" were only partly enriched by manganese. Evidently much of the ore in the Cason shale is of this type, and samples were accordingly taken to determine whether the material could be concentrated.

Concentration tests. - The ore from the unaltered opencut faces is hard, and the "buttons" do not shell out during crushing. Fracturing generally occurs through the "buttons" which contain on the average not more than 25 percent of manganese. A representative sample of the ore contained: manganese, 20 percent; iron, 7.5 percent; insoluble, 32.3 percent; and phosphorus, 0.32 percent.

Float-and-sink tests of hard, unweathered, Cason button-bearing shale showed that high-grade concentrates could not be made by gravity concentration. Ore sized between 35- and 65-mesh gave a heavy liquid (specific gravity, 2.92) concentrate assaying 26.8 percent manganese and 23.7 percent insoluble. When heavier liquids were used the percentage of manganese recovered decreased rapidly, and the grade of concentrate was not much improved.

Replacement Deposits in Fernvale Limestone. - Some manganese occurs in replacements in the Fernvale limestone, but the production has not been large. Where the Fernvale limestone outcrops disseminated manganese oxide can be seen. Samples of such material show that the manganese tenor was less than 5 percent.

The total amount of manganese in the Batesville district is large, but the tonnage of ores available under present mining and milling conditions is stated to be only about 420,000 tons. The amount of manganiferous clay probably runs into millions of tons, but the low manganese tenor of this material and the absence of any proved metallurgical process for its treatment make this material of doubtful value at present. The development of a low-cost treatment process would make these deposits valuable. Miser (260, p. 85), in quoting from his report of 1918 on the Batesville-Cushman district, states:

> An estimate of the quantity of available manganese ore of all grades in this region where mining is not preceded by systematic prospecting is difficult to make. Of the 180 deposits examined, about half contained an estimated available reserve of 200 tons or less. Only about one third contain 1,000 or more tons and only a few contain more than 5,000 tons, though certain of these contain many thousand tons. A small number of prospects and mines, however, were not visited, and these and the unexplored deposits may increase considerably the reserve. The deposits of the region perhaps include at least 250,000 tons of available ore containing 40 percent or more manganese and 170,000 tons of available ore containing less than 40 percent manganese.

In computing these figures Miser considers the cost of mining and preparing the ore for market and accordingly calculates a smaller tonnage of low-grade than of high-grade ore. Since this estimate was made new ore has been developed, but it is believed that the amount of new ore which can be concentrated does no more than offset the production from this district in the 13 years since Miser's estimate was made.

A fairly steady production of the same magnitude as in 1928 and 1929 probably can continue from the district for years to come if the value of ore remains at the price level prevailing during those years. The possibility of a large increase in production in the near future under normal conditions does not seem great, due largely to the failure of all attempts to put mining of the high-grade ores on an economic large-scale production basis and to the fact that much of the lower-grade ore will not respond to known methods of concentration.

Leadville District, Colo.

Colorado has been one of the larger producers of ores of manganese. Furness (105) estimates that the total production of the State up to and including 1925 has been 28,799 tons of manganese ore containing 35 or more percent manganese, and 3,088,078 tons of ore containing 5 to 35 percent manganese. Since that time Colorado has produced 85,852 tons (375) of ferruginous manganese ore, exclusive of fluxing ore, up to January 1, 1931.

The Leadville area has been the largest shipper of ores of manganese in Colorado. Much of it is of the ferruginous manganese type, and it is well-suited for the manufacture of spiegeleisen. During the war much of it was used to make a spiegeleisen with 33 percent manganese.

The chief producer of ferruginous manganese ore during recent years has been Cramer & Co., which operates the Star group of mines. During 1917 and 1918 this company produced about 250 tons of ore daily. Recent production has been 50 to 100 tons a day.

A representative analysis of ore from this property is: Manganese, 19.6 percent; iron, 20.4 percent; silica, 7.41 percent; phosphorus, 0.043 percent; and moisture, 17 percent. Ore from the Leadville district finds its market at the Pueblo (Colo.) plant of the Colorado Fuel & Iron Co.

Due to the inability to obtain representative samples of ore from this district no experimental work was done to see if the ore could be concentrated to a higher grade.

Cartersville District, Ga.

Location and Extent

For many years it has been known that numerous manganese deposits occur in northeastern Georgia, and the production of ores of manganese from that State is recorded as early as 1865. Of the several districts in this section the Cartersville area, near the town of the same name, has been the principal producer.

The ore deposits of the Cartersville district are found in a belt approximately 18 miles long and 1 to 2 miles wide. The longer axis extends north and northeast, the town of Cartersville lying just west of the district and about 4 miles from the southern boundary.

According to LaForge (172) workable manganese deposits are found in an area of about 30 square miles and occur in the clay and unconsolidated material resulting from the decay of the Weisner quartzite and Shady limestone.

Mineralogy

Various manganese minerals are found, the most common being psilomelane, pyrolusite, manganite, and wad. The greater part of the manganese is believed to occur as psilomelane, although in restricted localities pyrolusite predominates. The physical form in which manganese minerals occur range from soft powdery ore to hard nodular material, the latter predominating. With the manganese minerals in the residual clay varying amounts of cherty material are usually found. Limonite is commonly present and in some deposits is more abundant than the manganese oxides. Barite is present in some deposits, but the barium content of many ores is due to the barium content of the mineral psilomelane.

The largest production of manganese ores and ferruginous manganese ores during recent years has come from mines of the Georgia Manganese & Iron Co., which has been active in modernizing its mining methods and in the erection of a large modern mill, which was completed late in 1929. According to company officials this mill has a rated annual capacity of 200,000 tons of ore.

The ore is mined from open pits by hydraulic methods and washed to a central sump in the bottom of the pit, where coarse ore and rock are removed on a grizzly. Ore fine enough to pass the sump grizzlies is pumped to log washers for removal of clay. The granular material passes to the concentrator, where the coarser portion of the ore is jigged and the fines are tabled. During 1930 the mill produced approximately 12,000 tons of concentrates.

Concentration Tests

Gravity Concentration. - The production of manganese concentrates low enough in silica to meet metallurgical requirements is not unduly difficult. The manganese and gangue minerals are not intimately locked; and fine crushing, except on middling products, is not required. Before the new will was built some difficulty was experienced in the pilot plant in making satisfactory table concentrates. A study in 1928 of the table feed at Rolla indicated that if the ore were classified before tabling no great difficulty would be experienced. This problem is believed to have been solved satisfactorily in the new mill.

Magnetic Concentration. - Limonite is associated with the manganese oxides. It is particularly abundant in the upper portions of the deposits, and care is taken not to mine these irony zones. Some iron, however, is always associated with the ores and usually contaminates the mill concentrate. Limonite and other iron-bearing minerals are difficult to remove by jigs and tables. Inasmuch as ore having a ratio of less than 9 : 1 (preferably 10 : 1) parts of manganese to iron cannot be used for the manufacture of standard-grade--80 percent--ferromanganese considerable attention was given to a study of ore containing a greater ratio of iron to manganese than that mentioned. A brief general report on this phase of the manganese investigation was published in 1929 (68).

Although iron in manganese ores or concentrates is not penalized directly, the manganese in the ore is paid for on a sliding basis, with the result that an indirect penalty is in effect. For example, an ore containing 30 percent manganese and 20 percent iron may be paid for at a rate of 40 cents per unit of manganese, no credit being given for the iron content, whereas an ore containing 48 percent manganese and 5 percent iron will be worth 55 cents per unit. Therefore, the producer gains by shipping as high-grade a concentrate as possible.

The specific gravity of the limonitic grains in the Cartersville ores is 3.4 to 3.85, while that of the manganese particles is between 3.7 and 4.4. With such a small difference in specific gravity a clean separation between the two minerals cannot be made on jigs and tables. A roasting and magnetic process, therefore, seemed the only logical way to make the separation, and tests were accordingly made on the jig concentrates.

Six samples of jig concentrates were obtained from the pilot plant of the Georgia Manganese & Iron Co. in 1928. Each sample, which represented jig concentrates made at various times and on different types of ore, was given a reducing roast at 500°C. for 30 minutes. The roast converted the limonite into magnetic oxide (magnetite). After roasting the ore was quenched and separated for a magnetic and nonmagnetic product. No crushing was done before or after roasting. The results of these tests, given in table 9, show that the jig concentrates are particularly adapted to roasting and magnetic separation. From each sample a magnetic iron product and a nonmagnetic concentrate high in manganese and low in iron and well-suited for the manufacture of 80 percent ferromanganese were made. Fortunately the iron minerals are associated more closely with the phosphorus-bearing and siliceous minerals that are the manganese oxides. Thus, the manganese concentrate is lower than the roasted ore in both objectionable elements. The magnetic iron concentrate may be marketed as ferruginous manganese ore.

Some jig concentrates would not have to be submitted to a roasting and magnetic process. Much of the ore--for example, the first three jig concentrates in table 9--is so close to the required ferrograde that it could be mixed with the treated concentrates from more ferruginous ores, and the combined concentrates would still meet the requirements.

Magnetic separation would not supplant the jigging now in vogue, because the silica must first be eliminated. Free siliceous gangue particles in a gravity concentrate would pass into the nonmagnetic manganese product. The method does, however, make possible the production of a high-manganese, low-iron concentrate and would allow the operators to work ore bodies relatively high in iron, now neglected or wasted.

In brief, the Cartersville district of Georgia contains large bodies of ferruginous manganese ore in residual deposits that have as yet been only partly developed. A mining method whereby the ore can be removed from open pits by hydraulic methods has been successfully worked out. A modern mill was erected during 1929 and in 1930 produced about 12,000 tons of concentrates. The concentrates are suitable for many metallurgical uses, and laboratory work shows that the ferruginous concentrates sometimes produced can be converted to a high-grade ferromanganese ore and a manganiferous iron ore by roasting and magnetic separation.

Menominee District, Mich.

Location and Extent

The Menominee district, Mich., west of Escanaba, is primarily an iron-ore producer. However, in this area, as in other Lake Superior districts, manganiferous iron ores are present. The district also contains ferruginous manganese ores which, on account of their relatively high manganese content, were given attention.

Concentration Tests

These ores, which are high in manganese, are quite low in silica but high in phosphorus, therefore the purpose of the investigation was to determine if a high-grade manganese concentrate could be recovered low enough in phosphorus to be suitable for the manufacture of ferromanganese.

TABLE 9. - Roasting and Magnetic Test of Manganese Jig Concentrates

Approximate size, inch	Product	Weight, percent	Assay, percent				Percent of total			
			Mn	Fe	Insol.	P	Mn	Fe	Insol.	P
3/4	Unroasted ore	---	46.20	5.0	4.1	0.142	---	---	---	---
	Magnetic concentrate	7.8	29.3	27.9	8.6	.268	4.5	47.6	13.7	14.4
	Nonmagnetic concentrate	92.2	52.9	2.6	4.6	.136	95.5	52.4	86.3	85.6
	Composite	100.0	51.1	4.6	4.9	0.146	100.0	100.0	100.0	100.0
3/8	Unroasted ore	---	44.8	5.3	4.5	.141	---	---	---	---
	Magnetic concentrate	15.0	28.6	27.0	9.0	.227	5.5	74.9	27.4	24.0
	Nonmagnetic concentrate	85.0	52.2	1.6	4.2	.128	94.5	25.1	72.6	76.0
	Composite	100.0	48.7	5.4	5.0	0.143	100.0	100.0	100.0	100.0
3/16	Unroasted ore	---	44.8	6.3	3.7	.141	---	---	---	---
	Magnetic concentrate	5.1	14.4	44.9	4.3	.210	2.0	37.1	5.9	7.6
	Nonmagnetic concentrate	94.9	51.2	4.1	3.7	.140	98.0	62.9	94.1	92.4
	Composite	100.0	49.3	6.2	3.8	0.144	100.0	100.0	100.0	100.0
1	Unroasted ore	---	32.8	17.9	7.4	.170	---	---	---	---
	Magnetic concentrate	38.7	12.4	45.5	12.0	.259	13.2	92.6	60.7	58.1
	Nonmagnetic concentrate	61.3	51.7	2.3	5.0	.118	86.6	7.4	39.3	41.9
	Composite	100.0	36.5	19.0	7.8	0.173	100.0	100.0	100.0	100.0
1/2	Unroasted ore	---	31.2	16.8	10.2	.162	---	---	---	---
	Magnetic concentrate	30.9	4.0	55.2	12.7	.226	2.7	90.5	35.0	46.0
	Nonmagnetic concentrate	69.1	46.9	2.6	10.5	.119	97.3	9.5	65.0	54.0
	Composite	100.0	33.3	18.9	11.2	0.152	100.0	100.0	100.0	100.0
1/4	Unroasted ore	---	38.5	11.4	4.8	.130	---	---	---	---
	Magnetic concentrate	20.1	11.8	47.7	8.8	.199	5.5	82.8	31.7	30.1
	Nonmagnetic concentrate	79.9	51.0	2.5	4.8	.116	94.5	17.2	68.3	69.9
	Composite	100.0	43.1	11.6	5.6	0.133	100.0	100.0	100.0	100.0

A ferruginous manganese ore of the type described was obtained from the Judson mine of the Balkan Mining Co., Alpha, Mich. The analysis of the ore shipped by this company during 1929 follows (225): Iron, 35.29 percent; phosphorus, 0.745 percent; silica, 5.47 percent; manganese, 19.25 percent; alumina, 2.57 percent; calcium oxide, 2.33 percent; magnesia, 4.21 percent; sulphur, 0.075 percent; and loss on ignition, 4.62 percent.

The sample examined was approximately of the composition stated above. Visual examination showed that the manganese and iron minerals were locked and that crushing to at least 10-mesh would be necessary for any liberation. The manganese was present in oxide form, much of it being manganite. The iron was present as hematite. A screen analysis of the ore showed that the manganese minerals were harder than the hematite and tend to segregate in the coarser sizes.

Gravity concentration. - Float-and-sink tests were made of sized portions of the ore crushed to 10-mesh to determine whether phosphorus could be removed by a gravity process. A liquid with a density of 3.30 was selected so that if the phosphorus occurred as clean apatite (specific gravity, 3.15) it would be removed in the float. The examination indicated that gravity concentration would eliminate some of the phosphorus but that the greater proportion would remain locked with the iron and manganese. The degree of concentration of iron and manganese and the elimination of insoluble and phosphorus are shown in table 10.

Magnetic concentration. - A series of roasting and magnetic concentration tests was made to determine if the iron could be separated from the manganese minerals. A sample crushed to 10-mesh was given a reducing roast at 550°C. for 30 minutes. Tests with the Davis magnetic tube were made of a sample that had not been crushed after roasting, of a sample through 35-mesh, and of a sample through 100-mesh.

The results of these tests are given in table 11 and show how intimately the minerals are associated.

Upon crushing to 100-mesh, 61.1 percent of the manganese is still locked with the iron. The nonmagnetic product is high in manganese; the minus 100-mesh product has a tenor of 48.58 percent manganese. The phosphorus and insoluble tend to be segregated to about the same degree in the nonmagnetic portion.

To obtain more information on the occurrence of phosphorus two sized lots, 28- to 65-mesh and 65- to 150-mesh, were given a magnetic roast similar to that previously mentioned. Magnetic tube tests were then made of each lot. The nonmagnetic tailing from each size was then fractionated with a heavy liquid with a density of 3.30. The results are shown in table 12.

TABLE 10. - Float-and-Sink Tests of Judson Ore

Size, mesh	Product	Weight percent	Assay, percent				Percent of total			
			Mn	Fe	Insol.	P	Mn	Fe	Insol.	P
10 to 28.......	Float on 3.30.....	5.4	7.82	20.53	17.20	1.610	1.7	3.4	22.8	16.0
	Sink in 3.30......	94.6	25.37	33.73	3.32	.482	98.3	96.6	77.2	84.0
	Total.........	100.0	24.42	33.02	4.07	0.543	100.0	100.0	100.0	100.0
48 to 100......	Float on 3.30.....	7.4	7.70	18.85	24.52	1.720	2.7	4.0	34.0	22.0
	Sink in 3.30......	92.6	22.13	36.21	3.80	.485	97.3	96.0	66.0	78.0
	Total.........	100.0	21.06	34.92	5.33	0.576	100.0	100.0	100.0	100.0

TABLE 11. - Magnetic Tube Tests of Roasted Judson Ore

Size, mesh	Product	Weight percent	Assay, percent				Percent of total			
			Mn	Fe	Insol.	P	Mn	Fe	Insol.	P
Minus 10.......	Magnetic concentrate....	87.0	19.00	42.36	4.64	0.561	74.4	96.4	80.3	78.5
	Tailing...........	13.0	43.80	10.61	7.60	1.029	25.5	3.6	19.7	21.5
	Total.........	100.0	22.22	38.23	5.03	0.622	100.0	100.0	100.0	100.0
Minus 35.......	Magnetic concentrate....	84.7	17.87	42.56	5.40	.571	68.7	96.3	78.0	76.4
	Tailing...........	15.3	45.05	8.93	8.40	.973	31.3	3.7	22.0	23.6
	Total.........	100.0	22.02	37.42	5.86	0.632	100.0	100.0	100.0	100.0
Minus 100......	Magnetic concentrate....	82.3	16.41	45.04	4.40	.568	61.1	97.0	74.2	71.8
	Tailing...........	17.7	48.58	6.45	7.10	1.032	38.9	3.0	25.8	28.2
	Total.........	100.0	22.11	38.21	4.88	0.650	100.0	100.0	100.0	100.0

TABLE 12. - Roasting and Magnetic Tests Followed by Float and Sink Tests of Tube Tailings

Size, mesh	Product	Weight, percent	Assay, percent				Percent of total			
			Mn	Fe	Insol.	P	Mn	Fe	Insol.	P
28 to 65	Magnetic concentrate	86.0	18.93	41.86	4.80	0.57	69.6	97.1	79.7	85.2
	Tube tailing	14.0	50.77	7.60	7.50	.606	30.4	2.9	20.3	14.8
	Total .	100.0	23.39	37.06	5.18	0.576	100.0	100.0	100.0	100.0
	Tube tailing:									
	Float on 3.30	7.8	7.80	15.38	39.30	1.704	1.2	15.8	40.9	22.0
	Sink in 3.30	92.2	54.41	6.94	4.80	.513	98.8	84.2	59.1	78.0
	Total .	100.0	50.77	7.60	7.50	0.606	100.0	100.0	100.0	100.0
65 to 150	Magnetic concentrate	87.2	19.59	42.66	4.60	.582	70.8	97.9	80.2	86.7
	Tube tailing	12.8	52.12	6.10	7.73	.611	29.2	2.1	19.8	13.3
	Total .	100.0	22.83	37.99	5.00	0.586	100.0	100.0	100.0	100.0
	Tube tailing:									
	Float on 3.30	9.8	7.20	16.63	38.06	2.210	1.4	26.8	53.3	35.5
	Sink in 3.30	90.2	57.00	4.96	4.00	.437	98.6	73.2	46.7	64.5
	Total .	100.0	52.12	6.10	7.73	0.611	100.0	100.0	100.0	100.0

In the tests of 65- to 150-mesh material it was technically possible to produce a magnetic manganiferous iron concentrate assaying 42.66 percent iron, 18.59 percent manganese, 4.60 percent insoluble, and 0.582 percent phosphorus and also to produce a manganese concentrate with a content of 4.96 percent iron, 57.00 percent manganese, 4.00 percent insoluble, and 0.437 percent phosphorus. Unfortunately the high phosphorus content renders this concentrate useless for the manufacture of ferromanganese.

Cuyuna District, Minn.

Location and Extent

Its large reserves and production make the Cuyuna district, Minn., one of the more important manganese districts of the country. In 1928 and 1929 the production of manganiferous iron ores was approximately 1,000,000 tons annually. The annual production of ferruginous manganese ores during this same period was about 5,000 tons.

The district lies southwest of the Mesabi range and extends southwest 65 miles from Aitken through Crosby and Brainerd. The district is 1 to 12 miles wide. The area is of comparatively recent discovery, having been found by drilling areas that had been mapped by magnetic surveys. The surface of the district is rolling, and all ore bodies are covered by a heavy mantle of glacial drift. The occurrence of the manganese-bearing ore has been described by Zapffe (403).

Types of Ore

The manganese-bearing ores of the Cuyuna district may be grouped roughly into two classes. The most abundant ore is the low-silica, low-manganese, high-phosphorus type called brown ore. The other type is the so-called black ore, which is characterized by a higher manganese and silica content and by a lower phosphorus analysis than the brown ore. As a general rule the brown ore has less than 10 percent, but sometimes as high as 22 percent manganese is present.

Although many of the black ores have a relatively high iron content they are not merchantable on account of their high silica content. Ores of this type are frequently found in existing mines, and their concentration presents a pressing problem, because, should these mine workings be allowed to cave before this ore is removed, the cost of its recovery will be greatly increased. The concentration studies have accordingly been limited to the black ores.

Much of the data in the following pages has been taken from a previous report (67) published in 1930.

Mineralogy

The black ores consist of intimately associated iron, manganese, and gangue minerals. Hematite and psilomelane are the predominating ore minerals. Small quantities of manganite, pyrolusite, and limonite are also present. The hematite is usually of micaceous habit and occurs disseminated in widely varying proportions in quartz, carbonate minerals, and psilomelane. Psilomelane occurs disseminated in a manner similar to hematite, except that the psilomelane is usually in coarser grains.

The more important gangue minerals are quartz, feldspar, and mixed carbonates, quartz predominating. Feldspar occurs principally in large grains, sometimes partly replaced by psilomelane. The carbonates are often found as cementing material for fine quartz grains and for hematite, psilomelane, manganite, and pyrolusite particles. Calcite is the predominating carbonate, with minor amounts of rhodochrosite and siderite.

Much of the gangue may be characterized as a ferruginous chert. This material usually contains enough iron oxide to give it rather high specific gravity, making removal by gravity methods difficult. A further difficulty in ore testing is the similarity of the mineral and gangue grains, making visual examination almost futile; many chemical analyses are required.

Some idea of the close association of the manganese and iron minerals may be given by stating that on crushing to 325-mesh 40 percent of the manganese still remains locked with the iron. Upon crushing the manganese tends to concentrate in the coarser sizes, due to the hardness of the grains of high manganese content.

Concentration Tests

In a study of the characteristics of the ore to determine the degree of locking of the mineral and the grade of concentrate which could be made, various methods were employed. Microscopic examinations of polished sections were made. Roasting and magnetic concentration tests were performed, and detailed dissections of the ore were made by the use of heavy liquids.

Microscopic Examination. - Microscopic examinations were made of polished sections and the results recorded by photomicrographs and camera lucida drawings. Photomicrographs and camera lucida drawings are shown in figures 5, A and B, and 6, A and B, of briquets from two Cuyuna range ores. These figures show the extreme locking which exists between the mineral constituents of the ore. The results of this microscopic study have been given in detail in an earlier paper by Cooke and associates (58).

Float-and-Sink Tests. - Float-and-sink tests with various heavy liquids brought out many interesting facts. In general, they showed that the black ores have an appreciable amount of relatively clean mineral and also some clean gangue. Some of the gangue, however, is a ferruginous chert having a specific gravity not much less than that of manganese and iron oxides. The rejection of such heavy gangue material by gravity methods would be difficult. Float-and-sink tests of a representative ore are shown in table 13. This ore was crushed to pass a 4-mesh screen, and heavy liquid separations were made on sized samples. Material finer than 200-mesh was not treated. The results in table 13 represent the combined specific gravity fractions from 4- to 200-mesh. Material having a specific gravity greater than 4.0 assays 24.54 percent manganese, 34.98 percent iron, and 6.51 percent silica. This fraction contains 70.2 percent of the manganese and 51.0 percent of the iron. The presence of much locked material is indicated by the relatively large fraction having a specific gravity between 3.65 and 4.0 and it is made up partly of locked particles and to a greater extent of ferruginous chert. The material lighter than 3.0 consists mainly of clean gangue, the removal of which would be relatively easy with any gravity process.

Float-and-sink tests offer an excellent method of determining the association of gangue and the heavier manganese and iron minerals. The specific gravities of the iron and manganese minerals are, however, so nearly the same as to make this method impractical for determining the degree of grinding necessary to obtain a liberation between the iron and manganese minerals. This information was therefore found by roasting the ore to convert the iron oxides to magnetite, which was later removed magnetically.

Magnetic Concentration. - A sample was given a magnetic roast and then divided into six portions. Each portion was crushed to pass a certain screen, after which a magnetic separation was made. These tests, listed in table 14, show the extremely fine interlocking of the manganese and iron minerals. The degree of liberation progresses continuously as the size of ore particles decreases. Material crushed to pass a 14-mesh screen showed that only 15.83 percent of the manganese was liberated from the magnetic iron concentrate, whereas the sample crushed to pass 325-mesh showed liberation of 61.65 percent of the manganese.

The percentage of gangue in the magnetic concentrate also decreases in the finer sizes. The 14-mesh concentrate had 12.36 percent of insoluble, whereas the concentrate from the 325-mesh size contained 7.20 percent of insoluble. At 14-mesh, 48.61 percent of the insoluble is liberated from the iron concentrate. This amount increases progressively until at 325-mesh, 78.47 percent has been unlocked.

The manganese and iron minerals are associated so closely as to preclude the production of a concentrate of ferro grade by ore-dressing methods. It should be possible to make manganese concentrates considerably enriched in respect to the iron, but production of a concentrate containing 9 or 10 times as much manganese as iron, such as is required for a ferromanganese ore, seems impossible. The association of the silica with the valuable minerals in most of the ores examined is not as intimate as the manganese-iron combination, hence the production of concentrates low enough in silica for some metallurgical purposes seems possible.

Concentration by Classification and Tabling. - Without resorting to classification, good tabling results may be obtained on clean sulphide ores that have large differences between the specific gravities of the gangue and the mineral. On the other hand, due to the presence of heavy gangue particles and much locked mineral the Cuyuna ores present a difficult problem. For good concentration the ore must be well-classified before tabling is undertaken.

TABLE 13. - Float-and-Sink Tests of a Cuyuna Ore, 4 to 200-Mesh

Specific-gravity fraction	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	SiO_2	Mn	Fe	SiO_2
Float on 3.00	21.12	0.46	5.38	90.81	0.6	4.1	57.1
3.00 to 3.65	13.41	5.22	30.37	44.33	4.9	14.6	17.7
3.65 to 4.00	13.30	19.67	31.02	18.86	18.4	14.8	7.5
Sink in 4.00	40.67	24.54	34.98	6.51	70.2	51.0	7.9
Composite	88.50	15.12	26.60	34.21	94.1	84.5	90.2
Slime (minus 200-mesh)...	11.50	7.32	37.89	28.63	5.9	15.5	9.8
Total	100.00	14.23	27.90	33.57	100.0	100.0	100.0

TABLE 14. - Magnetizing Roast and Magnetic Separation Test of Minus 10-Mesh Ore Roasted at 550° C. for 30 Minutes

Size, mesh	Product	Weight, percent	Assay, percent				Percent of total		
			Mn	Fe	Insol.	SiO_2	Mn	Fe	Insol.
All through:									
14	Nonmagnetic tailing	18.3	14.26	6.86	52.20	- -	15.83	3.72	48.61
	Magnetic concentrate	81.7	16.98	39.69	12.36	- -	84.17	96.28	51.39
	Composite	100.0	16.48	33.68	19.65	- -	100.00	100.00	100.00
28	Nonmagnetic tailing	19.5	16.88	5.68	50.60	- -	19.71	3.31	50.91
	Magnetic concentrate	80.5	16.66	40.18	11.82	- -	80.29	96.69	49.09
	Composite	100.0	16.70	33.45	19.38	- -	100.00	100.00	100.00
48	Nonmagnetic tailing	22.0	18.06	5.78	48.40	- -	24.18	3.74	55.20
	Magnetic concentrate	78.0	15.97	41.94	11.08	- -	85.82	96.26	44.80
	Composite	100.0	16.43	33.98	19.29	- -	100.00	100.00	100.00
100..........	Nonmagnetic tailing	26.6	21.92	4.90	42.50	- -	35.31	3.82	59.56
	Magnetic concentrate	73.4	14.55	44.69	10.46	- -	64.69	96.18	40.44
	Composite	100.0	16.51	34.11	18.98	- -	100.00	100.00	100.00
200	Nonmagnetic tailing	36.0	23.45	5.29	38.80	- -	51.63	5.70	71.63
	Magnetic concentrate	64.0	12.36	49.20	8.64	- -	48.37	94.30	28.37
	Composite	100.0	16.35	33.39	19.50	- -	100.00	100.00	100.00
325	Nonmagnetic tailing	40.8	24.39	5.78	38.10	- -	61.65	7.03	78.47
	Magnetic concentrate	59.2	10.46	52.63	7.20	- -	38.35	92.97	21.53
	Composite	100.0	16.14	33.52	19.81	- -	100.00	100.00	100.00
	Unroasted ore	- -	15.04	32.14	20.76	18.62	- -	- -	- -

TABLE 15. - Table Concentration of 10-Mesh Classified Feed

Product	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	SiO_2	Mn	Fe	SiO_2
Table concentrates	54.79	20.87	34.62	9.74	72.07	59.98	27.20
Table tailings ...	24.29	10.92	23.86	33.73	16.72	18.32	41.78
Table feed	79.08	17.81	31.32	17.10	88.79	78.30	68.98
Slimes	20.92	8.50	32.80	29.08	11.21	21.70	31.02
Composite	100.00	15.86	31.63	19.61	100.00	100.00	100.00

Tabling certain of these ores has made a merchantable grade of concentrates with a fair recovery. Due to the necessity of fine grinding to obtain liberation, some of the ores, however, are not amenable to such treatment. The results of tabling one of the more amenable ores are shown in table 15.

The ore was crushed to 10-mesh and classified into four spigot products and a slime overflow. Each spigot product was tabled separately and a series of samples taken around the table. These cuts were later combined according to analysis, and for simplicity only the composite concentrates and tailings are shown. The combined concentrates represented 54.79 percent of the weight of the samples and had a tenor of 20.87 percent manganese, 34.62 percent iron, and 9.74 percent silica. Approximately 72.0 percent of the manganese and 60 percent of the iron were recovered. In this test a small laboratory table was used, and none of the middlings were re-treated. As already mentioned, a better recovery of manganese than iron is shown. A commercial plant would have the advantage of classifying the ore into a greater number of products of closer size, of using larger tables, and of grinding and recirculating middlings.

Upon crushing an ore to table size slimes are unavoidably produced, and unless some auxiliary method is available for the treatment of these slimes much mineral is lost. On some ores examined locking of the mineral was so intimate that grinding to at least 100-mesh would be necessary to give a concentrate of commercial grade. Flotation was accordingly tried on table slimes and on ores ground directly to flotation size.

Flotation. - A flotation test of a high-manganese nonmerchantable ore showed that a desirable concentrate could be made. The results are given in table 16. The concentrate contained 67.84 percent of the manganese and 53.11 percent of the iron. The middlings were not recleaned.

TABLE 16. - Flotation Test of a High-Manganese Ore

Product	Weight, percent	Assay percent			Percent of total		
		Mn	Fe	SiO_2	Mn	Fe	SiO_2
Cleaner concentrates...	53.4	29.16	25.53	9.77	67.84	53.11	26.87
Middlings.............	17.9	22.51	27.35	19.75	17.56	10.06	18.22
Rougher concentrates...	71.3	27.49	25.99	12.28	85.40	72.17	45.09
Rougher tailings.......	28.7	11.68	24.90	37.20	14.60	27.83	54.91
Composite.........	100.0	22.95	25.68	19.43	100.00	100.00	100.00

Reagents used	Pounds per ton of ore
Oleic acid.............	0.18
Sodium oleate..........	.50
Pine oil..............	.24
Sodium silicate.......	3.00
Sodium carbonate......	2.00

The reagents used evidently had little tendency to float the iron minerals since the iron analyses of the concentrates and tailings were nearly the same. It is thought that much of the iron that went into the concentrates did so solely because it was locked with manganese minerals; that is, the flotation is selective with respect to the manganese. The tendency of the manganese minerals to float is pronounced. The concentrates had 29.16 percent manganese, while analysis of the tailings showed only 11.60 percent.

Flotation requires the use of soft water. If hard water containing large quantities of calcium or magnesium salts is used the reagent consumption is increased due to precipitation of the oleates as insoluble calcium or magnesium oleates, and the time required for the frothing operation is also increased. With soft or treated waters the manganese minerals float fairly rapidly. Then the amount of reagents used decreases, and a more efficient separation can be made. Table 17 shows the results of a test of a Cuyuna ore, in which softened water was used.

Flotation offers a means of concentrating some ores which are so badly locked as to prevent a merchantable concentrate being made without fine grinding. Table 18 shows the results of float-and-sink tests of an ore of this nature sized between 35- and 65-mesh. The high silica content of the two heavier fractions indicates that there is little hope of obtaining a concentrate from this ore by tabling at 10-mesh. Actual tabling tests proved this point; the concentrates carried about 15 percent silica. Grinding to 100-mesh, however, liberated the mineral enough to allow a merchantable concentrate to be made by flotation. Flotation cannot, however, be used with success on all Cuyuna ores. A few of the ores examined are so complex that grinding to 100-mesh does not make possible the production of concentrates low enough in silica to be merchantable at present. One ore, which is representative of rather large reserves, responded to a tabling treatment but would not yield good-grade concentrates when the entire sample was ground to a fine size and floated. A microscopic study of this ore by Cooke previously mentioned (58) showed that the reason for this was the presence of a small amount of carbonate. This carbonate was very finely disseminated through siliceous gangue particles (see fig. 5, B), and since the reagents used in flotation tended to float carbonate minerals this siliceous carbonate was concentrated in the froth along with the manganese and iron minerals; hence, the resulting concentrates were too siliceous to be acceptable. An all-flotation process therefore could not be used on this ore, at least not with the reagents now in use. This ore can, however, be tabled first and the objectionable carbonate removed, after which the concentrates can be floated satisfactorily, as explained more fully in the following pages.

Combined Tabling and Flotation. - Some Cuyuna ores contain an appreciable amount of manganese and iron minerals recoverable at table size. It is logical to recover as much as possible of this coarse mineral without further grinding. Another point in favor of using tables instead of crushing direct to flotation size is that the flotation reagents so far used show little tendency to float the iron minerals, whereas some may be recovered by gravity. Consequently, tabling before flotation should materially increase the percentages of iron recovered.

TABLE 17. - Flotation Test, Using Treated Water

Product	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	SiO_2	Mn	Fe	SiO_2
Concentrates...........	73.4	21.80	37.07	8.20	88.69	80.08	33.08
Tailings...............	26.6	7.65	25.45	45.80	11.31	19.92	66.92
Composite.........	100.0	18.04	33.98	18.20	100.00	100.00	100.00

Reagents used	Pounds per ton of ore
Oleic acid..........	0.16
Sodium oleate.......	.50
Pine oil............	.08
Sodium carbonate....	3.00

TABLE 18. - Float-and-Sink Tests of a Cuyuna Ore, 35- to 65-Mesh

Specific-gravity fraction	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	Insol.	Mn	Fe	Insol.
Float on 2.95............	7.2	1.56	10.36	79.40	0.6	2.5	23.6
2.95 to 3.25.........	8.5	4.02	20.92	61.40	1.8	6.0	21.5
3.25 to 3.66.........	15.3	11.80	26.59	40.20	9.5	13.7	25.3
Sink in 3.66..........	69.0	24.30	33.37	10.40	77.8	88.1	29.6
Total.............	100.0	19.06	29.58	24.27	100.0	100.0	100.0

The ore used to determine the value of tabling before flotation was one of the most difficult of the Cuyuna ores examined. Previous larger-scale tests, in which the ore had been crushed to 8-mesh, classified into 10 spigot products, and then tabled, showed that the best concentrates obtainable at this size contained 14.6 percent of silica, clearly indicating the necessity of finer grinding. A sample of the ore was therefore ground to 65-mesh, then deslimed. The granular portion was tabled for concentrates, middlings, and tailings. The middlings were then reground and added to the slimes, which were then treated by flotation. The results of this test appear in table 19.

The table concentrates were somewhat higher-grade than the flotation concentrates, due partly to the cutting out on the table of the cleanest mineral, permitting all locked grains to pass into the middlings for regrinding and retreatment in the flotation cells.

Pilot Plant

As a result of this investigation a pilot plant consisting of 10 tables was built near Crosby, Minn., in the summer of 1930 to treat black ferruginous manganese ores. Results with this table plant have in general checked laboratory results.

TABLE 19. - Combined Tabling and Flotation Test

Product	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	SiO_2	Mn	Fe	SiO_2
Table concentrates......	28.8	23.29	36.01	8.84	37.43	33.51	11.18
Flotation concentrates..	31.3	22.72	33.60	12.57	39.68	33.98	17.30
Combined concentrates...	60.1	23.00	34.75	10.75	77.11	67.49	28.48
Table tailings..........	6.2	7.90	17.06	58.58	2.73	3.42	15.98
Flotation tailings......	33.7	10.71	26.71	37.46	20.16	29.09	55.54
Combined tailings.......	39.9	10.27	25.21	40.73	22.89	32.51	71.52
Composite..........	100.0	17.92	30.95	22.72	100.00	100.00	100.00

Reagents used in flotation test	Pounds per ton of ore
Oleic acid.........	0.20
Pine oil...........	.27
Sodium silicate....	6.00
Sodium carbonate...	5.00

A small flotation unit was also installed to treat the slimes from the table unit. The operation of the flotation unit was not entirely satisfactory, and more large-scale experimental work on this phase of the problem is needed.

This plant produced approximately 25,000 tons of concentrates during the summer of 1931.

Butte District, Mont.

Location and Extent

The Butte district, Mont., first attracted attention as a large potential producer of manganese during 1916 and 1917, when the price of manganese ore was high and the possibilities of obtaining large quantities of domestic ores were first considered. At a comparatively early date some oxidized ores were mined for their silver content, but the use of the black oxidized ore and the pink rhodochrosite ores was not considered seriously as a source of manganese until the beginning of the World War.

The production from this district in 1918 was 72,381 tons, of which the rhodochrosite contributed by far the greater amount. After the war period the mining and shipment of the rhodochrosite continued, but on a smaller scale. The development in 1927 of a process for calcining and nodulizing high-grade rhodochrosite ores constituted a distinct step in the metallurgical process of the district. The development in 1928 of flotation for concentrating the low-grade ores increased the reserves and has made possible production of the highest-grade metallurgical manganese ore in the world market.

The location of the Butte district is well-known to all mining men. Its general geology has been most fully discussed by Weed (381) and Sales (333). A study of the manganese deposits in particular has been made by Pardee (290). In discussing the occurrence and distribution of manganese Pardee (288, pp. 141-146, 174-176) says in part in his later report:

> ***. The lodes *** are formed along steeply pitching fractures in granite (quartz monzonite) and extend to great depths. Manganese minerals are widely distributed, both horizontally and vertically, but they are comparatively scarce in that part of the district known as the central copper zone and plentiful in an adjacent peripheral belt a mile or more wide called the silver-zinc zone.

Types of Ore

In general, two main types of manganese-bearing ores are found in the Butte lodes, the black oxidized ores near the surface and the pink carbonate and silicate ores that occur below. Pardee (293) says that the lower limit of the zone of oxidation does not extend more than 20 to 200 feet below the surface.

Oxide Ores. - Originally much fairly high-grade oxide ore was found in the outcrops but was largely mined in the early days. Lower-grade ore bodies containing 12 to 35 percent manganese occur, but they have never been opened to any extent as the ore has usually been too low-grade to be marketable, and concentration has not been successful. According to Pardee (288, pp. 173-174), the Butte district was estimated to contain, in 1917, 1,000 tons of high-grade ore (40 percent or more manganese) and about 400,000 tons of siliceous material. The high-grade ore was probably mined during 1918, but only a small part of the low-grade ore was mined.

The character of the oxide ores found in various parts of the district varies considerably, but in general the ores may be said to consist of particles of vein quartz cemented with or partly replaced by a variety of manganese oxides, pyrolusite predominating. The manganese minerals and the siliceous gangue are intimately mixed, making the production of a low-silica concentrate by ore-dressing methods extremely difficult.

Carbonate Ores. - Below the oxidized zone of the lodes in the manganiferous area of Butte the manganese occurs as rhodochrosite, with smaller amounts of manganese silicate (rhodonite). In places the rhodochrosite occurs almost free from impurities. From these ore bodies the high-grade ores--containing 35 percent or more of manganese--were mined during the war period and later were mined and calcined. The deposits of high-grade rhodochrosite ores have been found only in mines in the Black Chief vein. The Emma mine has been the chief producer, although the Ancient and Travona mines produced during 1917-1919. The total amount of high-grade rhodochrosite mined from 1917 through 1928 has been estimated at 230,000 tons.

In addition to the high-grade rhodochrosite deposits larger deposits of ore occur diluted with quartz, some rhodonite, and small amounts of galena, sphalerite, and pyrite. They also carry some silver. The proportions of rhodochrosite, rhodonite, and quartz vary throughout the various mines, and it is impossible to estimate with accuracy the manganese tenor of these deposits.

The occurrence of the low-grade ore is widespread; the amount is indicated by Pardee (288, p. 176), who, in 1921, after discussing the amount of high-grade carbonate ore in the district, said:

> *****. In addition the lodes contain an almost unlimited quantity of low-grade material consisting of the carbonate and silicate of manganese and quartz mixed in different proportions. This constitutes a reserve from which, if the necessity arose, the country's needs might be largely supplied. With improvements in the methods of reduction, much of it might even become valuable under ordinary conditions.

On account of the large amount, this low-grade ore has been given the most attention in the recent study of the Butte ores. The results of the experimental work on the oxides and carbonates follow.

Concentration Tests

Oxide Ores. - Much of the oxide ore is of low grade and not usable without concentration. Samples representative of much of the low-grade ore were obtained from outcrops of the Black Chief vein on the Travona claim. The lode was 100 to 150 feet wide. The samples represented 40 to 60 feet of the width. The ore is similar to that of the same vein which has been mined on the Ancient claim and may be deemed a counterpart of the material above the rhodochrosite ores of the Emma mine, where the oxidized zone is not observable.

The composite sample had 12.3 percent manganese, 2.4 percent iron, 75 percent insoluble, and 0.047 percent phosphorus. Much of the manganese occurred as pyrolusite, and the principal gangue mineral was quartz. Microscopic examination showed close interlocking of the manganese minerals and quartz and gave little hope that a low-silica concentrate could be obtained by ore-dressing methods.

Float-and-sink tests of a fraction sized between 20- and 35-mesh substantiated the results of the microscopic examination. The sink in a liquid with a specific gravity of 2.95 contained over 30 percent insoluble, largely silica.

The percentage of manganese in the average Butte oxide ore is low, and the association between the manganese and the quartz is such as to make it extremely difficult, if not impossible, to produce low-silica concentrates by ore-dressing methods. Some oxide deposits are known to be higher-grade and the ore somewhat cleaner, but the small tonnage of this material did not seem to justify further experimental work.

Carbonate Ores. - The low-grade carbonate ores occur as a mixture of rhodochrosite, quartz, and smaller amounts of rhodonite and sulphides. They have no value without concentration and accordingly were thoroughly examined.

Due to the size of the deposit of siliceous carbonate ore in the Emma mine, most of the research work was on ore from that property. A sample of ore requiring concentration was about half quartz; lead, zinc, and iron sulphides were also present. The rhodochrosite amounted to nearly 40 percent, so that the sample had about 20 percent manganese. The sample was taken across a 45-foot vein, no portion of which could be mined to produce a high-grade ore of 36 percent or more manganese content.

Some rhodochrosite occurred as clean pieces 1 inch or larger. Much of the quartz also was present in fairly large pieces. However, some of the quartz was finely disseminated through the rhodochrosite. Galena, sphalerite, and pyrite were found in small quantities, generally interlocked with the quartz. A small amount of rhodonite was also present.

At the beginning of the investigation the only available method for concentrating these ores seemed to be gravity concentration. However, research showed that high intensity magnetic concentration and flotation were applicable.

Gravity concentration. - Gravity concentration of this carbonate ore crushed through 10-mesh was only partly successful. The specific gravity of rhodochrosite is 3.6, and that of quartz is 2.65. The relative densities indicate that a separation should be obtained. However, even with classified feed, tables gave mediocre results with high-silica concentrates. One obstacle of gravity concentration is the fine dissemination of the quartz in the rhodochrosite and the interlocking of the sulphides and quartz. The latter condition is very troublesome because some composite grains have the same density as rhodochrosite. Gravity concentration does not appear promising as a method of treatment for the production of low-silica concentrates. It does, however, offer possibilities by removing some relatively clean quartz at table size, thus eliminating the necessity of grinding all of this resistant mineral to a fine size. Tests show that approximately 55 percent of the quartz can be eliminated by tabling 10-mesh material with a loss of only 12 percent of the manganese.

Magnetic concentration. - A search of the literature on magnetic concentration is not likely to lead one to try the process on rhodochrosite. Nevertheless, the sample examined was found to be decidedly permeable under a high-intensity magnet. Later on, the results of a test in a commercial laboratory on ore crushed through 20-mesh without the customary preliminary sizing showed that 32.1 percent of the ore could be obtained in a concentrate containing about 43 percent manganese and 6.5 percent silica. An additional recovery of manganese could be made by regrinding the middling product. The greater portion of the lead and zinc sulphides in the ore passes into the tailings. Experiments showed that rhodonite had almost the same magnetic permeability as rhodochrosite. Hence, magnetic separation of the two minerals is not possible. Ore containing any appreciable quantity of rhodonite therefore cannot be used, as the rhodonite passes into the concentrate and makes a siliceous product. If rhodonite is absent a high-intensity magnetic process will undoubtedly give a concentrate which after calcination will be suitable for metallurgical purposes. The objection remains, however, that the ore must be dried and sized before passing over the magnetic separator. The cost of such separators is relatively high, and the amount that each machine could handle would probably not average over a ton of feed per hour. The lead and zinc in the ore would be segregated in the tailing and could be recovered only by re-treating them by some other process.

Flotation. - In the course of the investigation a flotation method that resulted in an excellent separation between the various constituents of the ore was developed. The major part of the sulphides is readily recovered by the use of a small amount of xanthate, copper sulphate, and pine oil. The rhodochrosite is then floated by the addition of sodium oleate or oleic acid and pine oil. The quartz and rhodonite pass into the tailings.

The sulphide concentrates from a typical run had 3.0 percent manganese, 21.3 percent iron, 18.4 percent zinc, and 8.1 percent lead. Less than 1 percent of all the manganese was entrained in the sulphide concentrates.

The finished manganese concentrates made subsequently contained 67.7 percent of all the manganese and assayed 41.55 percent manganese. The tailing had less than 5 percent manganese and contained 10.8 percent of the total manganese in the sample. The middling had 27.35 percent manganese and represented 31.7 percent of the total manganese in the feed. In plant operation the amount of manganese recovered in the concentrates may be increased by part of the manganese in the middling; individual tests have shown that this product is amenable to further cleaning. The finished concentrates contained 6.9 percent insoluble matter, while the tailing included 89.8 percent insoluble. This result shows a decided selectivity. The results of this test and the reagents used are given in table 20.

Since the rhodonite passes into the tailings along with the quartz, manganese ores containing rhodonite can be concentrated readily by flotation.

The practicability of flotation for this ore has been proved by plant tests by the Anaconda Copper Mining Co. A summary of the results at this plant is taken from a current technical publication (84):

> Testing of flotation of rhodochrosite ore from the Emma mine of Butte Copper & Zinc at the plant of Anaconda Copper Mining at Anaconda, Mont., indicates that the method can be satisfactorily applied to this manganese-bearing ore. Since December 16, 1929, about 12,000 tons of rhodochrosite ore, averaging about 30 percent manganese and more than 20 percent silica, has been treated. The concentrate has averaged 38 to 40 percent manganese and less than 6 percent silica. The ore is now being treated at the rate of 300 tons daily, and about 200 tons of concentrate is being shipped to the Domestic Manganese & Development plant at Butte. This represents a recovery of about 95 percent of the manganese content of the ore. The nodulized product averages 60 percent manganese and 7 percent silica.

TABLE 20. - Flotation Test of Siliceous Carbonate Ore

Product	Weight, percent	Assay, percent					Percent, total				
		Mn	Fe	Insol.	Zn.	Pb.	Mn	Fe	Insol.	Zn.	Pb
Sulphide concentrate...	5.9	3.05	21.3	16.8	18.4	8.1	0.9	47.6	2.0	74.9	95.5
Manganese concentrate..	33.0	41.55	--	6.9	--	--	67.5	--	4.6	--	--
Middling..............	15.4	27.35	--	20.8	--	--	20.8	--	9.9	--	--
Tailings..............	45.7	4.78	--	10.8	--	--	10.8	--	83.5	--	--
Composite..........	100.0	20.03	--	49.2	--	--	100.0	--	100.0	--	--
Heads................	--	21.28	2.54	49.4	1.47	0.50	--	--	--	--	--

Reagents used	Pound per ton of ore
Sodium ethyl xanthate........	0.2
Copper sulphate..............	.5
Crude sodium oleate..........	1.0
Pine oil.....................	.4

W. B. Daly (61) manager of mines of the Anaconda Copper Mining Co., states that working out a flotation process for treatment of rhodochrosite ores in his company's mines has trebled the reserves of the Butte district. He also states that the cost of the flotation method will not exceed $1.50 per ton and probably will be $1.00. The value of the byproducts, lead, zinc, and silver, according to daly, more than offsets half of the milling cost.

Philipsburg District, Mont.

Location and Extent

The Philipsburg district 50 miles northwest of Butte is the chief producer of chemical-grade manganese ores in this country. Over a period of years this district has produced approximately 95 percent of the country's ores of this grade. Although a small tonnage of ore was shipped as early as 1900 substantial production did not begin until about 1916. During 1917 and 1918 the district produced 185,842 tons of ore, mostly for metallurgical purposes, which constituted approximately half the production of the entire country. During this period manufacturers of dry batteries used this ore in the absence of foreign ores, even though the percentage of available oxygen was less. The use of Philipsburg ore has therefore continued.

For the last several years the production of chemical ore from the district has been approximately 15,000 tons per year. Ore of this type commands substantial premiums over metallurgical ore, and more expensive concentration methods may be used to bring it up to grade. The value of the chemical ore shipped during the last few years has been approximately $40 per ton at the mine.

The Philipsburg district has been described in detail in a report by Emmons and Calkins of the United States Geological Survey (82).

The deposits of manganese ore that have been worked in the district are all in the oxidized zone. The oxidation is complete to a depth of 450 feet and probably extends to a maximum of 750 feet. Carbonate ore is believed to occur in large amounts in the unoxidized zones.

The general nature of the ores in the oxidized and unoxidized zones has been described in detail by Pardee (299, pp. 122-130). He states that the oxide ore consists of pyrolusite, together with smaller amounts of psilomelane, manganite, wad, and braunite. The gangue is mainly quartz, with some kaolin and smaller amounts of calcite and iron oxides. The unoxidized ore consists of a dense aggregate of rhodochrosite, with more or less quartz and a little pyrite or other sulphides.

Some high-grade oxide ores of shipping grade have been removed by selective mining, but in general it may be said that most of the ore requires concentration. The average ore as mined contains 30 to 38 percent manganese and 20 to 30 percent silica. The iron content of these ores is low, generally between 1 and 3 percent. Phosphorus is also low. The ores usually contain a small amount of silver, and although lead and zinc are sometimes found in small quantities the amount of copper is negligible.

Concentration Plants

A gravity mill employing jigs and tables was in operation in this district during 1918 but has since been abandoned. The method now in use for producing chemical-grade ore employs high-intensity magnetic separators. Two mills, the Trout and the Moorlight, have a daily capacity of approximately 100 tons apiece. Details of plant operation at both mills have been described in current publications (28, 96).

The flow sheet at both plants is essentially the same. At the Trout mill, which treats ore from the company mine, the run-of-mine ore is crushed to pass a 1½-inch grizzly. The crushed ore is conveyed to a Ruggles-Cole-type drier 30 feet long and 5 feet in diameter. The fuel used is nut-size coal. The drying operation reduces the moisture content of the ore 12 to 3 percent. The dust from the drier is caught in an 84-inch Cyclone dust collector. The dried ore is carried by a bucket elevator to a Leahy No-blind screen with 1/2-inch openings. The oversize is crushed by a set of 30-by-14-inch rolls operating in closed circuit with the screen. The screen undersize is ground to 6-mesh in a second set of 30-by-14-inch rolls, operated in closed circuit with a Colorado impact screen. This minus 6-mesh ore is sized further by a second Leahy screen into a plus 14-mesh product and a minus 14-mesh product. The sized ore then passes to storage bins of 200 tons capacity above the magnetic separators, where it is fed to three type 3-E Wetherill separators. Each separator has three magnets wound respectively with 30,000, 60,000 and 100,000 ampere turns and is operated with a direct electric current of about 120 volts. Concentrates are discharged into bins, whence they can be conveyed directly into railway cars.

Dust from dry crushers and screens is collected by housings connected with a second 84-inch Cyclone dust collector, placed over elevators and screens. This dust, and that collected during the drying operation, is wetted and tabled on a Plat-O slimer for a high-grade concentrate. Tailings from this operation are impounded, and those from the magnetic separators are placed on a storage dump. According to Furness (104, p. 188).

The ore treated contains from 30 to 35 percent manganese and 25 to 30 percent silica. Two and one-quarter tons of crude ore were required to make one ton of product containing 70 percent of manganese dioxide, less than 0.2 percent of phosphorus, less than 6 percent of iron, and approximately 10 percent of silica.

The flow sheet at the Moorlight mill, a custom mill, is much the same as at the Trout mill, except that the ore before being passed to magnetic separators is screened to produce 3 sizes instead of 2. At this plant no attempt is made to save the dust. The tailings are impounded,

The magnetic process as outlined yields a desirable product for the dry-battery industry. Tailings from the magnetic process contain about 20 percent manganese. Some of the ores contain impurities which would make them unsuitable for chemical purposes, and while they would be suitable for metallurgical purposes the lower value of this class of ore would not permit the treatment cost of a magnetic process.

Geologists who have examined the district agree that deposits of rhodochrosite ore, probably of large size, lie below the zone of oxidation. Treatment of such material constitutes a problem for the future.

Concentration Tests

In general it may be said that the higher-grade ores of the district can be adequately concentrated by the magnetic process now in use. The concentration problems of Philipsburg may therefore be said to deal with the following three classes of material:

(1) Oxide ores too low-grade to justify the use of the magnetic process and ores containing impurities which make them unfit for chemical purposes.

(2) Tailings from previous or present metallurgical processes.

(3) Unoxidized or carbonate ores.

During the investigation many samples of manganese oxide from Philipsburg material were examined. These samples included ores now being treated by the magnetic process, mill products, including tailings, now going to waste, low-grade dump ore, and ore not suitable for chemical purposes. Tests were made to determine the amenability of the various ores to gravity, magnetic, and flotation methods of separation.

Ore Unsuitable for Chemical Grade. - A sample containing approximately 35 percent manganese, 24 percent silica, and 4.5 percent lime, which on account of its physical and chemical characteristics was not suitable for chemical purposes, was examined. The manganese minerals in the ore consisted mainly of pyrolusite and psilomelane, and the gangue was mostly quartz. Microscopic examination showed that the manganese minerals were locked with the silica and that the production of a low-silica concentrate at a coarse size by any ore-dressing process was unlikely. Float-and-sink tests of this ore, followed by table tests, indicated that if it were crushed to 10-mesh, classified, and tabled, concentrates containing approximately 44 percent manganese and 12 percent silica could be made. Flotation tests gave unsatisfactory results. Pyrolusite is the most readily floatable of the oxide-manganese minerals, and as float-and-sink tests showed that manganese minerals upon grinding to 100-mesh had locked with them less than 7 percent silica, favorable results were therefore expected. A detailed study of the problem brought out the fact that the ore contained a large percentage of soluble salts which seriously interfered with the selectivity of the process. For this reason an all-flotation process on the oxide ores does not seem possible, although it is very probable that flotation would adequately handle the slime produced from table operations because much of the soluble salts would be washed out of the ore during crushing, tabling, and dewatering.

Tests of some of the low-grade ores indicate that their silica content can be reduced by gravity concentration. It is doubtful if the silica content can be reduced to the 8-percent limit required to make ferromanganese. Concentrates containing 12 to 15 percent silica can be made, and while such concentrates are not in demand now they could be used in emergency. The ratio of manganese to iron is satisfactory, and the phosphorus content seldom exceeds 0.15 percent.

Tailings. - During mining and milling dumps of sorted low-grade ore and mill tailings have accumulated which probably total 100,000 or 150,000 tons. The average analysis is not accurately known, although the tailings from the magnetic plants are said to contain 20 to 22 percent manganese. Samples from one dump contained about 39 percent manganese and 25 percent silica.

In 1927 some of the higher-grade dump ore was shipped to Utah, where it was used in the production of manganiferous pig iron. During 1927, 1928, 1929, and 1930 shipments of ferruginous manganese ores from Montana have been 10,332, 11,156, 15,665, and 11,875 tons, respectively, by years. Some of the higher-grade dump ore undoubtedly can be used in this way, but much of it is too low-grade to be marketable without concentration.

Examination of one of the higher-grade dump ores which contained 38.9 percent manganese, 1.6 percent iron, 26.6 percent insoluble, and 0.054 percent phosphorus showed that gravity concentration could grade this ore up to about 46 percent manganese and 14 percent silica.

Because these tailings are continually accumulating their treatment presents a problem. The samples studied had about 18 percent manganese, 2.1 percent iron, 58.4 percent insoluble, and 0.176 percent phosphorus. The liberated high-grade manganese minerals had been removed by the magnetic process, and the manganese minerals remaining in the tailings were badly locked with gangue. Float-and-sink tests, as well as high-intensity magnetic concentration of 20- to 35-mesh tailings, indicated that concentrates from either method would contain over 25 percent of silica. Finer grinding would undoubtedly result in somewhat cleaner concentrates.

According to Fitzberg (96), tailings from the Trout mill can be ground and re-treated by the magnetic process with an increase in the over-all recovery from 80 to 95 percent. However, manganese ore suitable for battery purposes must contain not more than a certain percentage of fines, and difficulty would be experienced in finding a market for such material. It seems probable, therefore, that the tailings will have to be ground so fine that they will be unsuitable for battery use. By sintering, however, these magnetic concentrates could be used for metallurgical purposes. Tabling of these tailings is not promising due to the fine grinding required and the resulting large slime loss. Flotation offers a possibility of treatment, although the presence of soluble salts has made results to date rather unsatisfactory.

Unoxidized Ores. - The deposits of manganese-bearing ores lying below the oxidized zone have not been opened to any extent, and samples of such material were not obtainable for tests.

Las Vegas District, Nev.

Location and Extent

In 1917 deposits of metallurgical manganese ores were discovered 16 miles east of Las Vegas, Nev., and about 5 miles west of the Colorado River. The discovery mine, the Three Kids, produced 15,045 tons of manganese ore in 1917 and 1918, but since that time the total production has amounted to less than 1,000 ton (104, p. 188). Due to consolidation of the Three Kids and Las Vegas groups the deposits of this area again attracted attention in 1929.

Mineralogy

The manganese-bearing deposits occur in low hills composed of volcanic flows and tuffs, gypsum, sand, and clay, which border the Colorado River. The manganese deposits have been formed by partial replacement of the tuffs and the sand and clay beds. The ore is a dark-brown fine-grained porous material of low specific gravity. Manganese is present mainly as wad, although small amounts of pyrolusite and occasionally psilomelane are found.

Concentration Tests

Records show that the ore shipped from the Three Kids mine contained 39 percent manganese, 11 percent silica, 1 percent iron, 0.3 percent phosphorus, and 10 percent moisture. The average grade of ore remaining in the district is leaner and requires concentration.

From the Las Vegas group of claims 12 samples requiring concentration were examined. These varied considerably in grade but had the same general character. Concentration tests of a composite sample only are reported.

This material had a tenor of approximately 24 percent manganese and 35 percent silica. The iron content was about 2 percent, and the phosphorus was low - 0.05 percent. This ore-bearing material consists of a pink clay and tuff which has been partly replaced by soft black amorphous manganese oxides, largely wad. The ore is quite porous and of light weight. At first appearance some of the ore seems fairly high-grade, but more thorough examination under the microscope shows that the original beds of clay and tuff have been only partly replaced by the manganese oxides. The amount of clean manganese mineral grains of any appreciable size was small. This preliminary examination was checked by float-and-sink tests which corroborated the evidence that the material would be difficult to concentrate.

The poor liberation of the gangue prevented concentration at 1/2 inch. Gravity concentrates of material sized between 1/2 inch and 10-mesh had a silica content of about 30 percent. When the ore was stage-crushed to 10-mesh approximately one third was finer than 100-mesh. Float-and-sink tests in table 21 show that gravity concentrates contain about 25 percent silica. The locking of the manganese and gangue in sizes as fine as 100-mesh and the presence of soluble salts prevented good flotation.

TABLE 21. - Float-and-Sink Tests of Las Vegas Ore

Mesh	Product	Weight, percent	Assay, percent			Percent of total		
			Mn	Fe	SiO_2	Mn	Fe	SiO_2
8 to 28.....	Float on 2.95..	25.2	12.72	2.3	51.20	11.8	26.1	40.3
	Sink in 2.95...	74.8	32.17	2.2	25.56	88.2	73.9	59.7
	Total.....	100.0	27.27	2.2	32.02	100.0	100.0	100.0
28 to 100...	Float on 2.95..	45.5	6.78	2.2	62.75	14.8	41.7	67.4
	Sink in 2.95...	54.5	32.66	2.6	25.30	85.2	58.3	32.6
	Total.....	100.0	20.88	2.4	42.34	100.0	100.0	100.0

Franklin Furnace, N. J.

The ores of Franklin Furnace, N. J., are mined primarily for their zinc content. They do, however, contain an appreciable amount of manganese, which is largely recovered in the residues from zinc smelting. These residues are smelted, and from them a large share of the country's spiegeleisen is produced.

The chief zinc minerals in these ores are franklinite, willemite, and zincite. Of these franklinite (Fe, Zn, Mn) O.(Fe, Mn)$_2$O$_3$, which contains 10 to 17 percent manganese, is most abundant. Concentration at the New Jersey Zinc Co. plant consists of removing the permeable franklinite by a magnetic process and recovering the other zinc minerals by gravity concentration. Smelting of the franklinite concentrates yields a residue having a composition similar to a ferruginous manganese ore.

The major part of the residues contains 12 to 14 percent manganese and approximately 40 percent iron. Material of this grade is used for the manufacture of spiegeleisen. The smaller part of the residues contains about 7 percent manganese and is used in the manufacture of pig iron. Statistics (104) for 1926 show that 74,096 tons of spiegeleisen were made from 149,374 tons of zinc residues containing 13 percent manganese. In this same year 11,219 tons of low-grade residues containing approximately 7.5 percent manganese were used in the manufacture of pig iron.

During the last 5 years an average of about 140,000 tons of zinc residues has been shipped from Franklin Furnace annually. Spiegeleisen has been made from this since 1870, and records of the material shipped from 1889 to 1930 show a production of approximately 4,000,000 tons.

Inasmuch as the manganese from this district is a byproduct in the smelting of zinc ores, speigeleisen can be produced at reasonable cost. These ore deposits apparently have a long life, and it is believed that an annual production of approximately 75,000 tons or more of speigel can be expected for many years. An additional smaller production of ore suitable for the manufacture of manganiferous pig iron may also be expected.

Little Florida Mountains, N. Mex.

Location and Extent

During recent years New Mexico has become of increasing importance as a producer of manganese ore. The greater part of the production has come from the Manganese Valley mine, on the east flank of the Little Florida Mountains, Luna County, about 16 miles east of Deming.

Associated with the high-grade metallurgical ores are lower-grade ores, some of which are being successfully concentrated. In addition to the ore body now being worked, somewhat similar deposits are found elsewhere along the same fissure.

The manganese-bearing ores occur in a fault fissure in agglomerate on the east side of the Little Florida Mountains, which are made up of agglomerate and felsitic rhyolite. The geology of the district is described by Furness (104, p. 120).

Mineralogy

Several types of ores of varying mineralogical content and structure are found. The manganese minerals are psilomelane, pyrolusite, manganite, and wad. The most important gangue constituent is a rhyolite, and the type of ore varies with the degree to which it has weathered. In some ores the rhyolite has decomposed to such an extent that little crushing is needed to give liberation. Other ores consist of a hard, unaltered breccia requiring fine grinding to free the manganese minerals.

Manganese Valley Mill

Ore mined from the Manganese Valley mine is trammed to the mill and dumped over a grizzly where the lump ore and waste are picked. Approximately 1 ton of lump ore is obtained from every 6 tons mined. The grizzly undersize constitutes the mill feed and contains about 22 percent manganese. Seven sizes are made, and by the use of storage hoppers the flow sheet is so adjusted that three jigs suffice. A representative analysis of 4,000 tons of concentrates shipped from this mine, according to Furness (104, p. 192), is as follows: Manganese, 45.75 percent; silica, 2.50 percent; iron, 2.0 percent; aluminum, 0.50 percent; copper, 0.078 percent; lead, 0.051 percent; calcium oxide, 5.50 percent; nickel, none; phosphorus pentoxide, trace; magnesium oxide, trace.

Concentration Tests. - No great difficulty has been experienced at the mill of the Manganese Valley mine in producing concentrates of satisfactory grade. The loss of manganese in the fines, however, has been considerable, although during the past year this trouble has been partly solved.

Some milling ore in the district is not so free from locked particles as that treated in the aforementioned mill, and concentration of such material will be more difficult. Particular attention was therefore given to the fine material lost by the method of concentration in use and to concentration of the so-called "frozen ores" — those requiring considerable crushing to free the manganese minerals from the gangue.

Until the early part of 1929 ores finer than one-fourth inch were not treated but were simply stock-piled, and at that time approximately 15,000 tons of such fines had accumulated. A representative sample was examined to determine whether it could be concentrated. The examination showed that much of the manganese was present as pyrolusite and psilomelane, with some wad. The gangue constituents were rhyolite, with some calcite. There was little locking of the manganese and gangue minerals.

Float-and-sink tests were made of various sizes to determine the grade of concentrates that could be produced by jigging or tabling. The results, given in table 22, show that with good operating conditions over 80 percent of the manganese should be recovered in the form of concentrates containing over 40 percent manganese and less than 6.0 percent silica.

TABLE 22. - Float-and-Sink Tests of Stock-Piled Mill Fines

Size, mesh	Product	Weight, percent	Assay, percent			Percent of total		
			Mn	Fe	Insol.	Mn	Fe	Insol.
1/4 inch to 10.	Float on 2.92..	53.1	4.6	2.2	68.6	11.3	48.9	92.8
	Sink in 2.92...	46.9	40.9	2.6	6.0	88.7	51.1	7.2
	Total......	100.0	21.6	2.4	39.3	100.0	100.0	100.0
10 to 35.......	Float on 2.92..	54.8	6.4	2.1	59.8	15.1	48.5	92.9
	Sink in 2.92...	45.2	43.7	2.7	5.5	84.9	51.5	7.1
	Total......	100.0	23.3	2.4	35.3	100.0	100.0	100.0
35 to 65.......	Float on 2.92..	53.8	4.8	2.3	64.7	12.6	37.3	89.8
	Sink in 2.92...	46.2	38.7	4.5	8.6	87.4	62.7	11.2
	Total......	100.0	20.5	3.3	38.8	100.0	100.0	100.0

The minus 1/4-inch material is now being treated at the Manganese Valley mine. It is deslimed in a spiral conveyor, and the coarse material is jigged. From the sizing analysis of the fines recovery probably could be increased by jigging the size coarser than 8-mesh and classifying and tabling the minus 8-mesh material.

Some fine pyrolusite will be lost, even by such a system, due to the tendency of this material to slime. Tests were accordingly made of a sample which broke readily and gave low recoveries in the mill due to slime losses. The chief manganese mineral in this sample was pyrolusite, with smaller amounts of psilomelane. The gangue constituent is a felsitic rhyolite.

Preliminary to gravity-concentration tests, two sizes, (1/2-inch to 10-mesh and 10- to 65-mesh) were fractionated with a heavy liquid having a specific gravity of 2.93. The results given in table 23 show that the ore is well-liberated at the sizes tested. Actual tabling tests of ore crushed to 10-mesh showed a recovery of only 60 percent of the manganese due to the large loss of manganese in the slime.

A flotation test, using the reagents listed on page 60, recovered a concentrate with a tenor of 45.6 percent manganese, 2.8 percent iron, and 9.2 percent insoluble. The percentage of manganese recovered was 64.5 percent. The middlings were not re-treated.

As has been mentioned, some of the ore in the district is more difficult to treat than that milled at the Manganese Valley mill. A sample of such ore from an ore body north of the present workings was examined. It was brecciated, and the gangue constituents were a felsitic rhyolite with a small amount of barite. The manganese occurs mainly as psilomelane, although some pyrolusite is also present. The specific gravity of the psilomelane is approximately 4.2 and that of the rhyolite 2.6.

TABLE 23. - Float-and-Sink Tests of Soft Ore

Mesh	Product	Weight, percent	Assay, percent			Percent of total		
			Mn	Fe	Insol.	Mn	Fe	Insol.
1/2 inch to 10.	Float on 2.93..	42.5	2.1	3.7	88.6	3.2	31.8	95.9
	Sink in 2.93...	57.5	46.5	5.9	2.8	96.8	68.2	4.1
	Total......	100.0	27.6	4.9	39.3	100.0	100.0	100.0
10 to 65.......	Float on 2.93..	34.3	1.7	2.7	86.3	2.1	15.4	87.3
	Sink in 2.93...	65.7	42.3	7.8	6.5	97.9	84.6	12.7
	Total......	100.0	28.4	6.0	33.9	100.0	100.0	100.0

Visual examination of the ore indicated that crushing to one-half inch would be required to liberate the gangue minerals.

Gravity concentration of this ore will be somewhat more difficult than that of the ores now being treated, as indicated by float-and-sink tests of ore sized between 1/2-inch and 10-mesh and from 10- to 35-mesh. Material coarser than 10-mesh yielded a sink product containing 13.4 percent of insoluble when fractionated with a heavy liquid of 2.95 specific gravity. These results are given in table 24.

The dissection of the 10- to 35-mesh size showed the presence of 10 percent of manganese in locked mineral of a specific gravity from 2.95 to 3.5. The heavy liquid fraction heavier than 3.5 contained 11.5 percent insoluble. The recovery of manganese is high, while the grade of concentrates is only fair.

The brecciated ores will be more difficult to treat than those now being mined, and the manganese content of the concentrates will be lower because of the presence of more locked gangue and also because of some associated barite. The percentage of iron and phosphorus in the concentrates will, however, be low.

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TABLE 24. - Float-and-Sink Tests of Hard Ores

Mesh	Product	Weight, percent	Assay, percent			Percent of total		
			Mn	Fe	Insol.	Mn	Fe	Insol.
1/2 inch to 10..	Float on 2.95..	45.6	4.1	2.4	84.9	7.7	60.5	84.1
	Sink in 2.95...	54.4	41.15	1.3	13.4	92.3	39.5	15.9
	Total.....	100.0	24.3	1.8	46.0	100.0	100.0	100.0
10 to 35.......	Float on 2.95..	47.0	2.4	1.9	88.2	5.7	46.4	80.2
	2.95 to 3.2....	6.9	8.5	1.7	58.9	3.0	5.7	7.9
	3.2 to 3.5.....	3.3	13.7	1.7	37.1	2.3	3.1	2.4
	Sink in 3.5....	42.8	41.3	2.0	11.5	89.0	44.8	9.5
	Total.....	100.0	19.9	1.9	51.7	100.0	100.0	100.0

Silver City District, N. Mex.

Location and Extent

Large shipments of ferruginous manganese ore during and since the war make the Silver City district of interest. Only a small quantity of high-grade manganese ore has been shipped from this area, but much ore suitable for the production of spiegeleisen has been mined.

Production figures of New Mexico, taken largely from Mineral Resources of the United States, show that from 1913 to 1929 the State produced roughly 350,000 tons of ferruginous manganese ore, the greater portion of which came from the Silver City district.

The most important deposits are on Boston Hill near Silver City. The deposits have been described by Wells (386) and by Goodier (120).

Mineralogy

The ore consists of an intimate association of iron and manganese oxides, occurring as fissure fillings and replacements in limestone. The chief ore minerals are pyrolusite and manganite, with some limonite and hematite. The ore ranges in color from dark red to black and is also of varying structure and hardness. Some of it is extremely hard and brittle, although some crumbles readily. Nodular ore is found in certain parts of the ore body. The iron and manganese minerals are closely intergrown and require fine grinding for liberation.

Concentration Tests

Samples of a ferruginous manganese ore and a siliceous ore were examined. Experiments were made with the ferruginous manganese ore to determine whether a high-manganese concentrate suitable for the manufacture of ferromanganese could be produced. The siliceous ore was examined to determine whether enough silica could be eliminated to make it marketable.

Ferruginous Manganese Ore. - An ore having the following analysis was examined: Iron, 33.67 percent; manganese, 16.81 percent; insoluble, 7.80 percent; silica, 5.48 percent; and phosphorus, 0.01 percent.

The ore was given a reducing roast at 550°C. for 30 minutes, then divided into three portions crushed to pass screens having 8, 28, and 100 meshes, respectively, per linear inch. Each size was then separated into a magnetic and a nonmagnetic portion by means of a Davis magnetic tube. The results, given in table 25, show the intimate association of the manganese and iron oxides. Even after grinding to 100-mesh, 43 percent of the manganese still remained locked with enough iron to render the mixture magnetic. The ratio of iron to manganese in all the nonmagnetic portions is too high to permit the material to be used in the manufacture of ferromanganese. Finer grinding of the roasted ore before concentration would undoubtedly increase the percentage of manganese liberated. Such fine grinding, however, in addition to the added cost would be undesirable in that it would produce a more siliceous manganese concentrate, since all the silica not locked with the iron particles would pass into the nonmagnetic product with the manganese minerals. The roasting and magnetic concentration process for treating such ores, therefore, is not promising.

The ore shipped to date has been of direct shipping grade, none having been concentrated. The average tenor of the ore from one of the larger mines, as given by Goodier (120), is reported as being 39 percent iron, 13 percent manganese, and 8 percent insoluble, the balance being largely lime. The phosphorus content is low, averaging about 0.012 percent. Estimates made in 1917 by Umpleby (374), when development work had not reached more than 40 feet below the surface, gave the district an ore reserve of at least 500,000 tons and possibly 1,000,000 tons of ore similar to that already mined.

Siliceous Ore. - The siliceous ore was similar to the ferruginous manganese ore, except that more free gangue was present. Although the ore bodies occur in a limestone formation the gangue mineral directly associated with the economic minerals in the low-grade ore looks quite unlike limestone. Apparently most of the original limestone has been replaced by silica and iron oxide, so that it has an appearance and chemical composition similar to a ferruginous chert. Visual examination of the ore indicated that the greater portion of the gangue would be liberated by crushing to ½-inch.

Float-and-sink tests of the ore sized between ½-inch and 10-mesh and 10- to 65-mesh were made. These separations, made with a heavy liquid with a specific gravity of 3.30, indicated that by jigging the coarser sizes and tabling the finer sizes concentrates containing about 36 percent iron, 12.50 percent manganese, and 9.2 percent silica could be made. The results are given in table 26.

Chamberlain District, S. Dak.

Location and Extent

Deposits of manganiferous material were discovered along the Missouri River near Chamberlain, S. Dak., in 1928. Because of their large size these deposits, although low in grade, have attracted much attention. Reports on the occurrence of manganese ore in this district are to be found in the current literature (83, 376).

TABLE 25. - Roasting and Magnetic Tube Test of Ferruginous Manganese Ore

Size, mesh	Product	Weight, percent	Assay, percent					Percent of total				
			Mn	Fe	Insol.	SiO_2	P	Mn	Fe	Insol.	SiO_2	P
Minus 8	(Concentrate	86.0	13.57	46.23	7.62	- -	- -	66.9	97.6	83.3	- -	- -
	(Tailing ...	14.0	41.32	7.04	9.36	- -	- -	33.1	2.4	16.7	- -	- -
	Composite	100.0	17.45	40.75	7.86	- -	- -	100.0	100.0	100.0	- -	- -
Minus 28	(Concentrate	81.7	12.82	47.52	7.46	- -	- -	60.4	96.9	69.6	- -	- -
	(Tailing ...	18.3	37.41	6.84	14.56	- -	- -	39.6	3.1	30.4	- -	- -
	Composite	100.0	17.32	40.07	8.75	- -	- -	100.0	100.0	100.0	- -	- -
Minus 100 ...	(Concentrate	72.4	11.13	52.87	5.72	4.30	0.010	43.2	94.3	48.1	50.65	50.0
	(Tailing ...	27.6	36.40	8.33	16.16	10.91	.027	56.8	3.7	51.9	49.35	50.0
	Composite	100.0	18.65	40.58	8.60	6.14	0.014	100.0	100.0	100.0	100.0	100.0

TABLE 26. - Float-and-Sink Tests of Siliceous Ore

		Weight, percent	Assay, percent			Percent of total		
Mesh	Product		Mn	Fe	SiO_2	Mn	Fe	SiO_2
1/2 inch to 10.	Float on 3.30..	40.7	3.51	13.73	52.50	16.3	20.8	79.9
	Sink in 3.30...	59.3	12.40	35.88	9.08	83.7	79.2	20.1
	Total......	100.0	8.78	26.87	26.75	100.0	100.0	100.0
10 to 65.......	Float on 3.30..	38.5	2.84	10.01	59.85	12.2	14.4	79.5
	Sink in 3.30...	61.5	12.71	37.31	9.68	87.8	85.6	20.5
	Total......	100.0	8.91	26.80	28.99	100.0	100.0	100.0

Manganese in this district is found as manganiferous iron carbonate nodules scattered through a bed of shale 35 to 40 feet thick. The manganese content of the bed of shale as a whole will average less than 2 percent. The nodules will average about 16 percent manganese and 8 percent iron.

According to the Interior Department press release just cited, the average yield of nodules from each yard of excavated material from 12 shafts on the property was 164 pounds. These nodules had an average analysis of 15.70 percent manganese and 11.08 percent iron; the phosphorus content is high, ranging from 0.38 to 0.55 percent; the silica and alumina contents were approximately 13 and 2.5 percent, respectively. A more detailed analysis of these nodules shows them to contain approximately 16 percent lime, 1.6 percent magnesia, and 0.05 percent sulphur, with a loss of about 25 percent on ignition.

Mineralogy

The manganese-bearing nodules consist of an isomorphous mixture of rhodochrosite, calcite, magnesite, and siderite. Fine grinding has given no indication of liberating the respective minerals. The specific gravity of the nodules is approximately 3.0 and the hardness about 3.5.

Concentration Tests

The dissemination of the minerals in the nodules as noted above was such that a brief examination showed ore dressing would be futile. Samples of the original material, consisting of the nodules in the shale, were not obtained, and the ease of separation of these nodules could not be tested.

The nodules are separated from the shale very easily by mere drying of the broken material in air for a few days. The procedure followed was that of breaking the ore bank, permitting it to stand a few days, and screening out the nodules which were then free from the shale. The manganese recovery by this procedure was very high (97.9 percent total). The surface of the deposit was covered with free nodules.

Northeast Tennessee District

Location and Extent

Numerous manganese mines and prospects are found in eastern Tennessee. They lie in a zone which extends diagonally across the state near its eastern border. Stose and Schrader (359), who examined the deposits in 1918, state that eastern Tennessee as a whole contains 130 or more mines or prospects. Although many deposits are known they are generally small, and no one has produced a large tonnage. Records from Mineral Resources of the United States show that the production of manganese ore from 1886 to the end of 1929 has been approximately 14,000 tons, and the production of ferruginous manganese ore during the same period about 5,000 tons. The district as a whole produced 6,206 tons of manganese ore and 2,158 tons of ferruginous manganese ore in 1917 and 1918. Since the war the annual production of high-grade ore has averaged less than 500 tons.

The chief manganese-producing area in eastern Tennessee, and the one that seems to have the greatest future, is in Johnson and Carter Counties, in the northeastern corner of the State. This discussion will therefore be devoted to the ores from this area. The deposits in these two counties are in the form of oxides scattered through residual clay or residual sand derived from the weathering of sedimentary rocks. According to Stose and Schrader (359):

> ***Most of the oxide ores may be classed as replacement deposits, some of them replacing the rock in place, but most of them replacing clay and sand, residual from rock decay, which still retain the rock structure. None of them except small amounts of ore associated with other deposits are believed to be strictly residual detrital deposits concentrated by gravity.

In this area the ore is found in residual deposits formed through the decay of the Shady dolomite and the Wantaga shale, (the first formation predominating.)

Mineralogy

Manganese is found in these deposits chiefly as psilomelane, which occurs as dense nodules, irregular fragments, and porous particles. The mineral is disseminated through clay. In some places, notably at the Cedar Hill mine, pockets of high-grade pyrolusite are found. Manganite and wad are also present in some of the deposits. Limonite is common in many of the ore bodies. Some of the limonite is in clean grains, but much of it is disseminated through the manganese particles. Gangue constituents associated with the clay are aggregates of quartz, weathered chert, and particles of sandstone.

Concentration Tests

Almost all the ore of the district requires some form of concentration. In the past, log washers were used to remove the clay; the log-washer concentrates were shipped without further concentration. For a few ores such a process makes a suitable product, but in the majority of the deposits the presence of chert and quartz, which are not removable, makes the log-washer concentrates too high in silica.

Gravity Concentration. - Examination indicated that the problem of concentration, particularly on ores from Carter County, was largely one of treating log-washer concentrates finer than one-half inch. Much of the clay can be eliminated from the ore by log washing, and fortunately the coarser portion of the ore consists of manganese oxides. Most of the chert and gangue particles are finer than one-half inch. The logical steps in the process are therefore log washing to remove clay, screening of the log-washer concentrates at approximately one-half inch for a coarse concentrate, and further concentration of the minus one-half inch material.

Samples of minus one-half inch washed material from 6 mines were examined in detail, but for the sake of brevity the results of the work on a composite made of samples from 5 of the 6 properties will be reported. An additional reason for so reporting the work is that the size of the individual deposits would not justify a separate mill, and as the mines are not far from each other the practical way to treat these ores would seem to be to log-wash the ore at each mine and send the log concentrates to a central plant for further treatment.

The composite sample had a tenor of 26.3 percent manganese, 12.4 percent iron, 29.0 percent insoluble residues, and 0.25 percent phosphorus.

Float-and-sink tests of sized portions of the ore showed that the mineral particles with a specific gravity greater than 3.2 contain 11.2 to 9.1 percent insoluble residues. The results are shown in table 27.

On first examination the mineral particles in these ores appear clean, but from the results they evidently contain an appreciable amount of very finely divided gangue. To determine the amount of silica in the apparently clean mineral a representative sample of 3-mesh ore was hand-picked; all particles of free gangue and all particles of manganese minerals to which gangue could be seen adhering were discarded. The specific gravities of the remaining apparently clean manganese minerals were determined with a Joly balance, then the particles were combined according to their specific gravities. The results of the assays given in table 28 show that the silica content varies in a general way with the specific gravity; the presence of both iron and manganese and the porosity of the mineral cause some irregularities. The greater portion of the limonitic grains is only slightly lower in specific gravity than the cleanest manganese particles, thus it is obvious that they cannot be removed by jigging or tabling without causing an excessive loss of manganese.

These results have particular interest, because many manganese ores found in residual deposits throughout Virginia and Tennessee show similar characteristics; that is, particles of apparently clean psilomelane vary in specific gravity from little more than that of the gangue to over 4.0 and contain amounts of silica up to 25 percent. With such ores, concentration is difficult, and the operator must choose between a small recovery of a high-grade concentrate or a greater recovery of a siliceous concentrate. Fine grinding of such material has little value, since the gangue particles are so small and so scattered through the manganese oxide that they are not liberated by grinding to 100-mesh.

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TABLE 27. - Float-and-Sink Test of Composite Sample, Minus 1/2-Inch Log-Washer Concentrate

Size, mesh	Product	Weight, percent	Assay, percent			Percent of total		
			Mn	Fe	Insol.	Mn	Fe	Insol.
1/2 inch to 4.	Float on 3.20..	39.2	11.0	17.7	47.4	16.0	48.5	73.2
	Sink in 3.20..	60.8	37.0	12.1	11.2	84.0	51.5	26.8
	Total.....	100.0	26.8	14.3	25.4	100.0	100.0	100.0
4 to 10.......	Float on 3.20..	35.2	9.4	13.0	58.3	11.8	38.5	77.2
	Sink in 3.20..	64.8	37.9	11.2	9.3	88.2	61.5	22.8
	Total.....	100.0	27.9	11.8	26.5	100.0	100.0	100.0
10 to 65......	Float on 3.20..	45.1	7.8	8.4	70.0	14.5	36.8	86.3
	Sink in 3.20..	54.9	38.0	11.5	9.1	85.5	63.2	13.7
	Total.....	100.0	24.4	10.1	36.5	100.0	100.0	100.0

TABLE 28. - Specific-Gravity Analysis of Hand-Sorted Concentrate, Through 1/2-Inch

Specific gravity	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	Insol.	Mn	Fe	Insol.
3.0 to 3.2............	4.9	0.5	41.7	22.8	0.1	14.0	6.9
3.2 to 3.3............	9.0	15.6	25.5	24.5	4.3	16.1	13.6
3.3 to 3.4............	15.0	36.0	12.1	12.8	16.8	12.6	11.9
3.4 to 3.5............	6.7	.9	38.2	35.6	.3	18.2	15.0
3.5 to 3.6............	11.8	14.9	28.3	24.9	5.6	23.1	18.2
3.6 to 3.7............	7.5	42.4	6.1	13.3	9.9	3.5	6.3
3.7 to 3.8............	30.6	43.1	4.1	12.0	40.9	9.0	23.1
3.8 to 3.9............	14.5	48.8	3.3	5.5	22.1	3.5	5.0
Composite........	100.0	32.2	14.3	16.0	100.0	100.0	100.0

The foregoing statements indicate that the minus one-half inch portion of this ore is difficult to concentrate. The coarser portion is, however, clean enough so that the low-grade concentrates obtainable from the finer sizes may be mixed with it and a marketable product produced. Such concentrates would contain too much iron, silica, and phosphorus to be used for ferromanganese but could be used for other metallurgical purposes.

Magnetic Concentration. - Preliminary magnetic tests gave encouragement. The cooperation of the Dings Magnetic Separator Co. of Milwaukee, Wis., was obtained.

A sample of the composite log-washer concentrate was crushed to pass 12-mesh and given several passes through a high-intensity magnetic separator. Either the strength of the magnetic field or the belt speed was varied for each pass. From the results in table 29 it may be seen that a small proportion of the iron mineral is highly magnetic and can be removed with a low-intensity magnetic field that will not affect the manganese. However, after this small amount of iron, which is mainly magnetite, is removed no clean-cut separation can be effected between limonite and the manganese minerals. Contrary to expectations, the limonite was slightly less magnetic than psilomelane. A good separation was made between the manganese minerals and the free siliceous particles. The silica in the manganese concentrates was locked. The analyses of the magnetic manganese concentrates compared closely to the heavier material obtained by fractionating a like size sample with a heavy liquid of 2.90 specific gravity.

These tests are interesting primarily to show the characteristics of the ore. High-intensity separation has been found practical for the concentration of chemical grade ore in the Philipsburg (Mont.) district, but it has as yet not proved economical for the production of metallurgical ore at present prices.

TABLE 29. - High Intensity Magnetic Test of Composite Sample, Minus 12-mesh Log-Washer Concentrate

Magnetic intensity	Belt speed, f.p.m.	Current, amperes	Weight, percent	Assay, percent			Percent of total		
				Mn	Fe	Insol.	Mn	Fe	Insol.
Low........	75	0.5	1.7	2.4	47.2	20.7	0.2	6.0	1.3
Medium.....	75	1.5	5.5	39.3	9.9	8.8	8.1	4.0	1.8
Medium high	75	2.0	35.0	37.1	11.8	10.7	48.9	30.8	13.7
High.......	75	2.5	23.5	32.4	15.1	13.4	28.7	26.5	11.5
Extreme....	50	2.5	15.0	21.6	20.6	23.2	12.2	23.1	12.8
Nonmagnetic	50	2.5	19.3	2.6	6.7	83.2	1.9	9.6	58.9
Total..	--	--	100.0	26.5	13.4	27.3	100.0	100.0	100.0

Roasting and magnetic tests were made of jig concentrates to produce a high-grade ore suitable for ferromanganese. This gravity concentrate, sized between 1/2-inch and 10-mesh, was given a reducing roast and the ore separated into magnetic and nonmagnetic portions. The results, given in table 30, indicate that a high-manganese, low-iron concentrate can be produced. The phosphorus and silica are shown to be associated more closely with the iron than with the manganese particles. However, the phosphorus content of the manganese concentrate is still high (0.325 percent), rendering the material unusable for the manufacture of ferromanganese.

TABLE 30. - Roasting and Magnetic Test of Minus 1/2-Inch C Plus 10-Mesh Composite Gravity Concentrate

Product	Weight, percent	Assay, percent				Percent of total			
		Mn	Fe	Insol.	P	Mn	Fe	Insol.	P
Magnetic concentrate...	43.5	23.2	31.5	14.3	0.554	37.5	84.0	50.5	56.7
Nonmagnetic concentrate	56.5	49.1	4.6	10.8	.325	62.5	16.0	49.5	43.3
Composite.........	100.0	37.8	16.3	12.3	.425	100.0	100.0	100.0	100.0

Flotation. - Flotation tests met with some success, although difficulty was experienced in overcoming the ill effects of the slimed iron oxides, which tended to cause dirty concentrates. The results of one test in which the ore was ground to 100-mesh, after which the finest slimes were removed before flotation, are shown in table 31.

Grinding log-washer concentrates for flotation does not seem justified. It is believed that concentrates of satisfactory grade can be made by jigging and tabling at lower cost.

A particular field for the use of the flotation process does, however, exist. Large amounts of fine manganese minerals, largely pyrolusite, are lost in log washing. Where the size of the operation justifies the expenditure, some of this fine pyrolusite can be recovered by reclaiming the heavier portion of the log-washer overflows in thickeners or settling ponds and re-treating this material by flotation. Samples from a settling pond at the Cedar Creek mill were tested by flotation. They were taken at the edge of the pond and are undoubtedly enriched by selective settling, nevertheless the test indicates the floatability of the mineral. The sample - assaying 25.3 percent manganese, 23.7 percent iron, 13.8 percent insoluble residues, and 0.251 percent phosphorus - was treated by flotation, and fair recovery of concentrates was made with a tenor of 42.9 percent manganese, 22.5 percent iron, and 2.5 percent insoluble residues. The type of reagents and the amounts used were similar to those shown in table 31.

TABLE 31. - Flotation Test of Composite Log-Washer Concentrates

Product	Weight, percent	Assay, percent		Percent of total	
		Mn	SiO_2	Mn	SiO_2
Cleaner concentrate.....	63.0	32.16	13.17	72.75	36.95
Cleaner tailings........	3.9	14.41	39.45	2.00	7.98
Rougher concentrate.....	66.9	31.17	15.08	74.75	44.95
Rougher tailings........	33.1	21.30	37.35	25.25	55.07
Composite..........	100.0	27.90	22.45	100.00	100.00

	Pounds per ton ore		
Reagents used	Rougher	Cleaner	Total
Pine oil..............	0.06	0.06	0.12
Oleic acid............	.18	.09	.27
Sodium silicate.......	2.00	1.50	3.50
Sodium carbonate......	1.00	.50	1.50
Sodium oleate.........	.05	---	.05

Blue Ridge Region, Va.

Location and Extent

Virginia, the first producer of manganese ore, has numerous deposits in a belt paralleling the Appalachians and extending from the northern to the southwestern part of the State.

Before the World War Virginia produced 45 percent of the total manganese ore mined in this country. The greater portion of the 270,348 tons of ore produced in Virginia from 1867 to 1917 came from the Crimora mine. Since 1917 Virginia has produced, according to Mineral Resources of the United States, up to and including 1929, 48,436 tons of manganese ore, 23,638 tons of ferruginous manganese ore, and 5,094 tons of manganiferous iron ore (360).

The manganese deposits have been examined by geologists of the United States Geological Survey and the Virginia Geological Survey; and two excellent reports (358,360) have been published since 1918, in which the geology and the various deposits are described.

Most manganese ore of this district is found as residual deposits, resulting from the decay of the Shady dolomite. About 82 properties of this nature were described by Stose and his associated in their report (360).

A discussion of only some ores found in the Blue Ridge region will be given here. The deposits of the Oriskany formation, Woodstock district, will be discussed later.

Mineralogy

The ore is usually found as masses of oxides disseminated through clay. The predominant manganese mineral is psilomelane, with smaller amounts of manganite, pyrolusite, and wad. The psilomelane usually is in nodular form; much of it has a dull luster, indicating a high gangue content. Some of the manganese mineral also occurs as flat, shaly particles of light weight and low grade. Associated with the clay in some ores are particles of chert and shale.

Concentration Tests

Exploratory work during recent years has indicated the presence of ore at the Old Dominion property. Inasmuch as this deposit adjoins the Crimora mine, which produced approximately 160,000 tons of high-grade ore, samples from the Old Dominion mine were given particular attention.

Gravity Concentration. - A composite sample from drill holes on the Old Dominion property was examined. Much manganese was in the form of psilomelane nodules, although some of it occurred as flat shaly appearing particles. The clay had been washed out of the sample, so that the product examined may be said to correspond to a log-washer concentrate. The gangue consisted largely of altered chert with some shale. Much psilomelane had a dull luster and apparently contained considerable silica. This was brought out by a detailed examination and will be discussed in some detail later. A screen analysis, given in table 32, shows that the manganese in this ore, as in other residual ores, has a decided tendency to segregate in the coarser sizes.

Float-and-sink tests of fine sizes indicated that unless many of the lower-grade manganese-mineral particles could be rejected in the tailing gravity-concentration methods would yield siliceous concentrates and lower recovery. The results of these tests appear in table 33.

The experiments indicated that the manganese mineral contained much gangue so finely disseminated that it was not detectable with the naked eye or the low-power microscope. The percentages of gangue in the seemingly clean manganese particles varied widely. To determine the percentage of clean mineral and the relation between the specific gravity and gangue content of the mineral grains, the density of each particle of a sample of plus 3-mesh material was determined with a Joly balance. The free gangue and the visibly locked grains were removed before the test was begun. After the specific-gravity determinations the particles were combined into respective specific-gravity increments and analyzed. The results are shown in table 34.

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TABLE 32. - Screen Analysis of Old Dominion Ore

	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	Insol.	Mn	Fe	Insol.
Plus 4 .	18.5	30.5	6.3	33.8	23.9	18.1	14.1
4 to 14	53.2	26.0	6.7	38.9	58.6	55.0	46.8
14 to 100 . .	25.5	15.8	6.0	59.5	17.1	23.7	34.4
Minus 100 . .	2.8	3.6	7.5	63.6	.4	3.2	4.7
Composite	100.0	23.6	6.5	44.2	100.0	100.0	100.0

TABLE 33. - Float-and-Sink Tests of Old Dominion Ore

esh	Product	Weight, percent	Assay, percent			Percent of total		
			Mn	Fe	Insol.	Mn	Fe	Insol.
4 to 14..	(Float on 2.92	30.9	5.9	3.5	80.6	6.9	16.4	64.1
	(Sink in 2.92	69.1	34.9	8.2	20.3	93.1	83.6	35.9
	Total	100.0	26.0	6.7	38.9	100.0	100.0	100.0
20 to 35.	(Float on 2.92	43.5	4.1	2.6	86.8	8.9	16.0	76.4
	(2.92 to 3.2	9.6	20.8	9.3	42.7	10.0	13.0	8.3
	(3.2 to 3.5	13.1	21.7	15.9	29.0	14.3	30.4	7.6
	(Sink in 3.5	33.8	39.4	8.4	11.3	66.8	40.6	7.7
	Total	100.0	19.9	6.9	49.4	100.0	100.0	100.0

TABLE 34. - Specific-Gravity Analysis of Manganiferous Ore from Old Dominion Mine

Specific gravity	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	Insol.	Mn	Fe	Insol.
2.9 to 3.0	1.4	28.1	2.5	41.0	1.0	1.0	2.9
3.0 to 3.1	6.6	33.3	2.5	32.2	5.4	4.4	10.6
3.1 to 3.2	8.1	35.3	1.8	29.4	7.1	4.0	11.9
3.2 to 3.3	4.7	33.7	2.3	31.2	3.9	2.9	7.3
3.3 to 3.4	14.0	35.6	5.9	25.1	12.3	22.2	17.5
3.4 to 3.5	6.9	42.7	4.0	15.4	7.3	7.3	5.3
3.5 to 3.6	7.5	41.5	2.7	18.9	7.7	5.4	7.1
3.6 to 3.7	5.4	41.8	3.2	17.3	5.6	4.7	4.7
3.7 to 3.8	34.6	43.9	2.9	17.0	37.5	26.7	29.3
3.8 to 3.9	3.3	44.9	5.3	10.0	3.7	4.6	1.6
3.9 to 4.0	6.6	44.9	9.1	5.3	7.3	16.1	1.7
4.0 to 4.1	.9	54.0	3.0	1.4	1.2	.7	.1
Total ..	100.0	40.5	3.7	20.0	100.0	100.0	100.0

TABLE 35. - Float-and-Sink Test of ½-Inch to 10-Mesh
Old Dominion Ore

Product	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	Insol.	Mn	Fe	Insol.
Float on 2.95	29.8	4.6	2.6	85.4	4.7	14.3	72.3
Sink in 2.95	70.2	39.8	6.6	13.9	95.3	85.7	27.7
Total	100.0	29.3	5.4	35.2	100.0	100.0	100.0

TABLE 36. - Float-and-Sink Test of 20- to 35-Mesh
Page County Ore

Product	Weight, percent	Assay, percent			Percent of total		
		Mn	Fe	Insol.	Mn	Fe	Insol.
Float on 2.95	8.9	1.6	3.2	89.2	0.4	8.0	31.4
2.95 to 3.2	4.9	20.1	5.9	43.6	2.7	8.0	8.2
3.2 to 3.5	12.5	30.4	4.2	30.0	10.5	15.0	14.5
Sink in 3.5	73.7	42.5	3.3	16.3	86.4	69.0	45.9
Total	100.0	36.2	3.5	26.1	100.0	100.0	100.0

TABLE 37. - Flotation Test of Old Dominion Ore

Product	Weight, percent	Assay, percent		Percent of total	
		Mn	SiO_2	Mn	SiO_2
Cleaner concentrates	47.8	35.62	12.65	80.00	14.80
Cleaner tailings (middlings)	6.9	11.62	51.00	3.70	8.60
Tailings	45.3	7.64	69.05	16.30	76.60
Composite	100.0	21.28	40.85	100.00	100.00

Reagents used	Pounds per ton		
	Cleaner	Rougher	Total
Oleic acid	0.12	0.06	0.18
Sodium oleate ..	.24	.06	.30
Pine oil	.12	-	.12
Sodium silicate.	2.00	1.00	3.00
Sodium carbonate.	1.00	.50	1.50

Many of the particles of low specific gravity were flat and shaly. The grains of better grade were of a nodular shape, but except the heaviest, they also contained too much silica.

Some of the ore from the Old Dominion property does not contain so much shaly manganese material, as shown by examination of another sample that is more favorably inclined to concentration. A float-and-sink test of it is shown in table 35.

The presence of much silica in apparently clean psilomelane grains is common in the residual deposits of the Appalachians. Ores of similar character are found in other Virginia deposits and in Tennessee, as has been reported previously.

A float-and-sink test of an ore from Page County, Va. (table 36) shows the large amount of gangue contained in nodules of psilomelane, which to the naked eye are free of gangue. Apparently this condition is due to partial replacement of siliceous gangue mineral by manganese oxides. Grinding to extremely fine size is necessary to unlock the manganese minerals.

Attention is called to the fact that the assays for insoluble residues, which include both silica and alumina, have been shown in the preceding tests. These ores contain much alumina, hence the silica analyses are generally several points lower than the insoluble analyses. Cleaner ores than those just cited are believed to be present in the Blue Ridge region, however, it is apparent that many of the ores are made up largely of low-grade manganese minerals that will not yield concentrates containing less than about 12 percent silica. Such concentrates, while not attractive to producers of ferromanganese at present, would, however, find a ready market for blast-furnace use and could also be utilized for the production of a 70 percent ferromanganese during emergencies.

Flotation. - Several flotation tests of Old Domion ore gave fair results. Grinding to 150-mesh did not give complete liberation, and the flotation concentrates had a tenor of about 13 percent of silica. The results of a typical test and the reagents used are given in table 37, and indicate a recovery of 80 percent of the manganese. This ore, however, floated quite slowly, and the advisability of applying flotation to ores of this type is still open to question.

Woodstock District, Va. (358)

Location and Extent

Because of the development of a large ore body and the erection of a modern mill at the Mineral Ridge or Cedar Creek property the Woodstock district requires attention. The ore formation is also somewhat different from the residual manganese deposits commonly found in the Appalachian region.

Among the manganese properties in the Woodstock district the Cedar Creek is outstanding. This property is on Manganese Ridge 11 miles north of Woodstock, Va., and has an interesting history. Manganese ore was first produced there in

1834, and the mine has been operated intermittently ever since. The production of ore in the earlier days was small, and the methods of mining and preparation were crude. Hand sorting and log washing were practiced. Estimates place the total production until April 1921 as 4,000 tons. The property was acquired in 1920 by the Hy-Grade Manganese Production & Sales Corporation, which has since carried out an exploration program. Production until 1930 came largely from the development work. Some of the ore was hand-picked and the rest treated in a small jigging and tabling plant. The value of the output up to 1928, according to C. W. Massie, manager of the property, was $300,000. By 1929 exploration had proved the existence of a large ore body. A detailed geological survey of the property was made in 1920 by Stose and Miser.

Mineralogy

Pyrolusite and psilomelane are the most important manganese minerals, although some manganite and wad are also present. At some places pyrolusite accounts for most of the manganese, while at others psilomelane predominates. The pyrolusite is high grade, and much has been hand-picked and shipped during previous years for chemical ore. It is usually fine-grained and crumbles to a fine powder when handled. Psilomelane in the ore usually is found as nodules with a botryoidal surface and contains an appreciable amount of barium oxide. Manganite often is found as radiating crystals associated with the pyrolusite and psilomelane. Very little wad was seen in the samples examined, but according to Stose and Miser some of it occurs disseminated through pyrolusite and is said to contain 40 to 45 percent manganese. Associated with the manganese minerals are quantities of sandstone, chert, quartz, and clay and varying amounts of limonite. The phosphorus content of the ore shipped from this property has been 0.20 to 0.25 percent.

Concentration Tests

A study of the ore from the Cedar Creek mine indicates that a concentration process would consist of two steps, (1) washing the clay from the mixture of manganese oxides and chert and (2) separating this chert from the economic minerals. Because much of the manganese is in the form of soft, powdery pyrolusite which slimes badly, precautions must be taken to recover as much of the fine mineral as possible. Separation of the coarse minerals from the gangue is not particularly difficult. The ore is not badly locked, and crushing to one-half inch is sufficient. The predominant gangue mineral other than clay is a weathered chert of quite light weight; tests showed that it had a specific gravity of 2.15 to 2.62. In general, the specific gravity of the manganese minerals is more than 4, so that there is ample difference between the weights of the manganese and gangue to permit separation of the two with jigs and tables.

Cedar Creek Mill

Construction of a modern mill, with a rated capacity of 30,000 tons of ferro-grade ore per year, was begun in 1929 by the Hy-Grade Manganese Production & Sales Corporation and completed late in January 1930. Inasmuch as this mill is the newest in the country and embodies modern methods of concentration the flow sheet (fig. 7) will be discussed in some detail.

Because the general character of the ore treated is much the same as that in residual manganese deposits throughout the Appalachians, the same general flow sheet, with small changes to take care of the peculiarities of each ore, will no doubt be found applicable to other ores.

The ore is trammed to the mill grizzly, which has openings of about 4.5 inches. The oversize is low-grade and is rejected, and the undersize constitutes the mill feed.

The mill feed passes to a trommel with 1¼-inch holes, where the screening is done without the addition of water. The undersize is washed in an Elmore washer to remove the clay. The washed material passes to a set of rolls, where it is crushed to one-half inch. The trommel oversize is crushed separately in a gyratory crusher.

The minus one-half inch feed is screened into 4 sizes by Hum-mer screens, and each of the 3 coarser sizes is treated separately on Harz-type jigs. The finest size and the undersize from the Elmore washer are deslimed in a Dorr classifier. The flow sheet shows the sand from the Dorr classifier distributed to three tables. A change has since been made so that the sand product passes to a hydraulic classifier, and a classified feed is fed to the tables.

Middlings from the jig are ground in a Hardinge ball mill and pumped back to the Elmore washer for re-treatment. The hutch product from the Harz jigs, plus the table middlings, are re-treated in a James jig. Slimes from the Dorr classifier and the hydraulic classifier are dewatered by three cones and concentrated on two slime tables.

The advantage of feeding a classified product to tables instead of a distributed feed was brought out well at this mill. Installation of a multiple-spigot classifier resulted in an increase in the capacity of the tables and a decrease in the manganese content of the table tailings from about 11 to about 2 percent compared to results with a distributed feed.

The metallurgical results at this mill are quite satisfactory; the concentrates are suitable for metallurgical purposes, and the recovery of manganese is high considering the type of ore treated. It might be added that the company also hand-picks and cobs some of the ore in the open pit to produce a che chemical grade product. The output of the mill, except a small tonnage ground by the company for use in the ceramic industry, is consumed by steel plants.

Olympic Peninsula, Wash.

Location and Extent

For many years, manganese-bearing ores have been known to occur in the Olympic peninsula; but little attention was given to them until the discovery in 1923 of the Crescent mine, which has produced high-grade metallurgical ore. Since that time prospecting has been done, and outcrops of manganese deposits have been discovered; however, none contain as high-grade ore as that produced by the Crescent mine.

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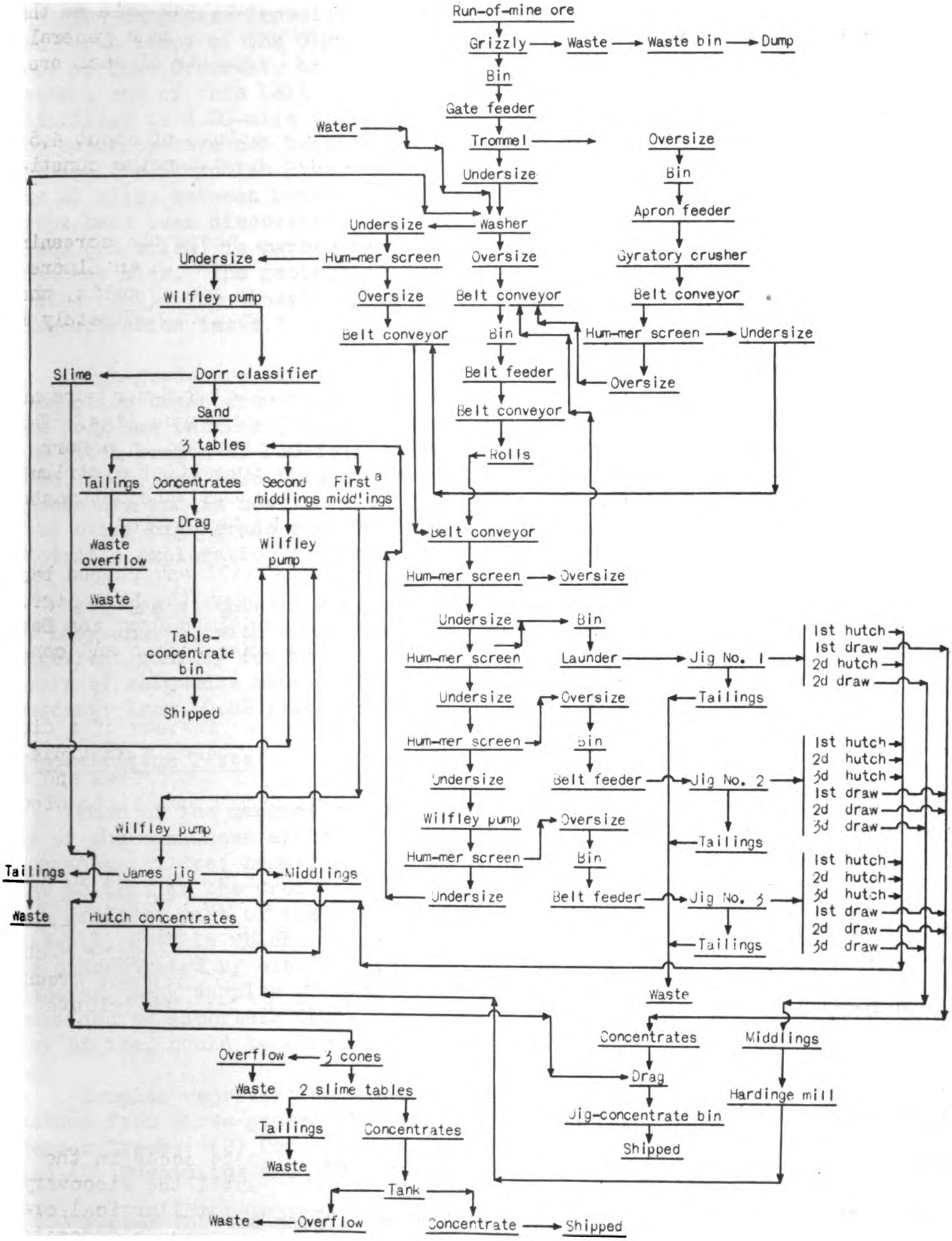

[a] First middlings nearest concentrate.

Figure 7.—Flow sheet of Hy-Grade Manganese Production and Sales Corporation, Cedar Creek Mill, Woodstock, Va.

The manganese deposits occur in a belt extending around the south, east, and north sides of the Olympic Mountains from near Humptulips to Beaver Creek, west of Lake Crescent, or 110 miles. The Humptulips deposits are at the southwestern end of this belt. Between these deposits and the South Fork of Skokomish River is a 20-mile stretch where manganiferous float has been found, but the outcrops have not been located. A number of mines and prospects are located between the Skokomish River and Mount Constance, a distance of 25 miles. In the 20 miles between Mount Constance and Lake Crescent a few manganiferous outcrops have been discovered. The area between Lake Crescent westward to Beaver Creek (25 miles) is marked by well-distributed outcrops, including that of the Crescent mine. The geology of the district has been described in detail by Pardee (289). The mineralogy of the various ore deposits will be discussed under "Concentration tests."

High-grade ore was discovered a mile west of Lake Crescent in 1923; and production began from this property, known as the Crescent mine, in 1924. The ore body was tabular (6 to 14 feet thick) and almost vertical. It had a maximum pitch length of 180 feet and a maximum slope length of 120 feet. During 1924, 1925, and 1926 this ore body produced 16,275 long tons of high-grade manganese ore and is now thought to be worked out. Efforts of the operators to find other high-grade ores at this mine have not been successful, although considerable exploration has been done.

The ore at this mine consisted of a hard, dense mixture made up principally of hausmannite, with some bementite and a manganiferous carbonate. It was of excellent quality for metallurgical purposes, as is shown by the following analysis of shipments made in 1924, aggregating about 5,000 tons: Manganese, 52.88 percent; iron, 0.83 percent; silica, 8.80 percent; and phosphorus, 0.05 percent.

Concentration Tests

Much of the manganiferous material in the Olympic Peninsula consists largely of the manganese silicates, bementite predominating, with minor amounts of manganese oxides, hematite, and quartz. Small deposits of high-grade ore similar to that at the Crescent mine may be found, but it is evident that by far the greatest part of the manganese is in the form of siliceous material. Obviously, ores in which the manganese is chemically combined with silica cannot be concentrated by ore-dressing methods to produce low-silica concentrates. However, many samples of manganiferous ores from outcrops of the district were examined to ascertain their composition and character and to determine whether any of them could be cleaned by ore-dressing methods.

Samples representing the manganiferous deposits of the district were obtained from three general localities: (1) Crescent area (Lake Crescent to Beaver Creek); (2) Constance area (approximately 13 miles west of Brinnon); and (3) Humptulips area (Humptulips River Basin, 30 miles north of Hoquiam).

Except for the sample taken from the Crescent tunnel all were from surface trenches, no underground workings having been opened. Inasmuch as weathering has not altered the deposits more than a foot or so below the surface it is believed that the manganiferous deposits will not vary greatly at depth from the samples obtained by trenching. The analyses of the samples and the approximate locality from which they came are given in table 38.

TABLE 38. - Locations and Analyses of Manganiferous Material from Olympic Peninsula

District	Assay, percent				Description of sample
	Mn	Fe	Insol.	P	
Crescent....	35.9	1.6	22.5	0.041	General sample from 3 surface showings
	48.3	.4	15.5	.058	Selected high-grade specimens
	44.8	1.7	16.1	--	State lease claim
	26.2	3.2	21.9	--	Low-grade ore from Crescent tunnel
Constance...	31.2	17.1	16.3	.079	Elkhorn claims
	45.4	4.9	22.9	.083	Achilles property
	10.7	23.9	37.4	--	3 showings, east lead claim No. 4
	26.7	9.9	37.1	--	Middle lead claim No. 6
	20.8	21.6	22.9	--	West lead claim No. 15
	28.4	18.9	21.8	--	General sample
Humptulips..	14.4	21.6	40.9	.062	General sample of outcrop ore
	36.6	2.0	27.0	.050	Selected high-grade specimens
	11.4	32.7	24.6	--	Hand specimens of typical ore

The material from all three districts is similar. The manganese occurs as a silicate, and the phosphorus content is uniformly low. The ore from the Crescent district is characterized by its relatively high manganese and low iron contents. Ore from the Constance area is somewhat lower in manganese and higher in iron. The Humptulips ore usually contains considerable hematite and is relatively low in manganese.

Crescent Area. - Examination of the general sample from this district showed that it was made up of a fine-grained aggregate of hausmannite and bementite and a complex manganese carbonate. Little free gangue was present, and float-and-sink tests showed virtually no separation. A sample from the State lease claim was the only one which responded to gravity concentration. This sample was hausmannite and a relatively light-weight manganese silicate. Float-and-sink tests of this material gave a concentrate containing only 4.8 percent insoluble. The results of these tests, with those of the Crescent tunnel sample (which proved to be similar to the general sample, except that it contained more bementite and manganese carbonate), are given in table 39.

No separation could be made of any of the three samples by magnetic methods, virtually the entire sample in each case being attracted by a high-intensity magnet.

Constance Area. - Most of the ore from this district was hard and brittle and broke with a conchoidal fracture. Bementite was the predominant mineral, but a considerable amount of dense reddish mineral with a vitreous luster and a specific gravity of 3.1 was also present. This was assumed to be neotocite.

TABLE 39. - Float-and-Sink Concentration of 20- to 35-Mesh Olympic Peninsula Manganese Ores with Heavy Liquid of 2.95 Specific Gravity

Sample	Feed, percent			Concentrates, percent				Tailings, percent			Recovered Mn, percent	Rejected Fe, percent	Rejected insol., percent
	Mn	Fe	Insol.	Weight, percent	Mn	Fe	Insol.	Mn	Fe	Insol.			
Crescent area:													
General sample ...	38.1	2.7	22.5	93.8	39.2	2.6	22.0	21.0	3.6	29.1	96.6	8.3	8.0
State lease	44.3	1.4	15.9	65.5	53.3	1.0	4.8	27.1	2.2	37.0	78.9	53.5	80.2
Crescent tunnel ..	25.9	4.7	20.6	85.7	27.9	3.6	20.7	13.9	4.0	20.4	92.3	12.1	14.2
Constance area:													
Elkhorn	- -	- -	15.3	98.8	30.0	19.3	15.2	- -	- -	22.9	- -	- -	- -
Achilles	45.0	- -	23.3	97.1	45.5	2.7	23.1	28.8	- -	29.3	- -	- -	- -
East lead	11.1	24.2	36.2	84.9	11.4	27.0	30.3	9.9	8.4	69.4	86.6	5.3	28.9
Middle lead	27.0	10.7	37.4	64.2	38.2	13.6	15.0	7.1	5.7	76.6	90.6	19.1	74.1
West lead	20.8	21.5	23.0	92.5	20.4	22.6	22.3	26.0	7.5	31.2	90.7	2.6	10.1
General sample ...	28.2	19.9	21.2	91.5	29.1	21.3	18.5	19.0	6.2	50.5	94.3	2.6	20.3
Humptulips area:													
General sample ...	14.6	20.8	40.5	62.7	17.2	26.7	28.4	10.3	10.9	60.9	73.6	19.6	56.1
Hand specimens ...	11.3	32.7	23.1	79.8	12.2	34.2	20.5	7.6	26.1	33.3	86.4	16.2	29.1

Little free gangue could be observed, and the presence of iron in the oxide form could not be detected by the eye. In many ways these ores resemble a slag both in appearance and in the manner in which the mineral constituents occur. Float-and-sink tests of samples of these ores, sized between 20-and 35-mesh, were very unpromising, only one ore giving a concentrate as low as 15 percent insoluble (see table 39). Two of the samples contained material that was strongly magnetic and could be separated with a hand magnet. The remainder of the material was attracted by a high-intensity magnet. The strongly magnetic portions were the higher in iron, and it is probable that they contained some magnetite particles of minute size, although none were detected.

Humptulips Area. - The samples from this area contained considerable hematite and appeared to have a much higher manganese content than the chemical analyses showed. The illusion is due to the formation of superficial oxide coatings along fracture planes; and as the ore breaks along these fractures many of the particles appear to be solid manganese oxides, while in reality all but the outer film of high-grade oxide consists of manganese silicates.

Float-and-sink tests of two samples showed that some enrichment could be made by gravity concentration but that in all probability the concentrates would contain not less than 20 percent silica. The results are shown in table 39.

Approximately 10 percent of the composite sample was strongly magnetic, 84 percent was weakly magnetic, and the remaining 6 percent was nonmagnetic. The strongly magnetic material is higher in manganese and lower in iron than the weakly magnetic portion. This strongly magnetic condition can only be explained by assuming that the higher-grade manganese oxides are associated with a small amount of magnetite. The iron mineral in the weakly magnetic portion is undoubtedly hematite. The results of magnetic tests are shown in table 40.

TABLE 40. - Magnetic Concentration of Some Olympic Manganese Ores, 20- to 35-mesh

Sample	Magnetic intensity[1]	Weight, percent	Assay, percent			Percent of total		
			Mn	Fe	Insol.	Mn	Fe	Insol.
Constance (middle lead)	Strongly magnetic..	23.4	33.1	16.9	12.1	26.5	31.3	13.6
	Weakly magnetic....	74.8	28.7	11.6	22.2	73.5	68.7	79.9
	Nonmagnetic........	1.8	---	---	74.4	---	---	6.5
	Total.........	100.0	29.2	12.6	20.8	100.0	100.0	100.0
Constance (general sample)	Strongly magnetic..	32.3	25.0	23.0	20.1	28.5	45.3	28.1
	Weakly magnetic....	67.7	29.9	13.2	24.5	71.5	54.7	71.9
	Total.........	100.0	28.3	16.4	23.1	100.0	100.0	100.0
Humptulips (general sample)	Strongly magnetic..	10.4	30.8	14.1	15.4	15.8	8.2	5.5
	Weakly magnetic....	83.8	20.3	19.1	27.0	83.9	88.9	78.4
	Nonmagnetic........	5.8	1.0	9.1	80.2	.3	2.9	16.1
	Total.........	100.0	18.6	18.4	30.5	100.0	100.0	100.0

[1] The strongly magnetic material was removed with a hand magnet, while the weakly magnetic material was removed with a high-intensity magnet.

SUMMARY AND CONCLUSIONS

The supply of domestic manganese ore having over 35 percent of manganese in the crude state is not great, but the present investigation indicates that the tonnage of ore that can be concentrated to this grade is large.

In the course of an investigation by the United States Bureau of Mines 116 ores from 20 States were examined to determine their amenability to concentration. A description of 17 of the more important manganese deposits, with experimental work on ores from them, is reported in some detail. These individual reports show the character of the ores and give results indicative of what may be expected by concentration. Of the 116 ores examined, 20 may be concentrated to meet all requirements for ore suitable for the manufacture of standard 80-percent ferromanganese, and 43 were found of suitable composition for use in the production of spiegeleisen or high-manganese pig iron.

During the investigation a flotation method for the treatment of both carbonate and oxide ores was developed. This process depends on selective flotation of the manganese oxide and carbonate minerals away from the gangue by the use of fatty acids of fatty acid soaps and suitable conditioning agents, such as sodium silicate, and a frothing agent. For most ores an alkaline circuit is necessary, but in some instances the use of a slightly acid circuit in the cleaning stages is desirable. This process is especially applicable to the treatment of the low-grade carbonate ores of the Butte district. The Anaconda Copper Mining Co. has demonstrated successfully the practicability of the flotation of these ores and has produced low-phosphorus concentrates which when sintered have 60 to 62 percent manganese and about 7 percent silica. The cost of milling ores by this process, according to company officials, is $1.00 to $1.50 per ton, and the by-product value of the metallics recovered incident to the flotation of the manganese will compensate for about half of this cost.

Particular attention has been given the ferruginous manganese ores of the Cuyuna district, Minn. The close association of the iron and manganese minerals prevents the production of ferro-grade ores from such material by existing ore-dressing methods. However, much of the silica can be eliminated by these methods, making the ore suitable for other metallurgical purposes. A 30-percent spiegeleisen is probably the highest alloy of manganese that can be manufactured directly from the concentrates.

In the summer of 1930 a 10-table pilot plant with a supplementary flotation unit was built and operated at Crosby, Minn. It demonstrated that certain manganiferous ores of that district could be concentrated. During the summer of 1931 this plant produced approximately 25,000 tons of concentrate containing less than 10 percent silica from ore formerly regarded as untreatable.

Due to the physical and chemical nature of the ores, the concentration of the large low-grade deposits of the Chamberlain (S. Dak.) and the Kingman (Ariz.) districts by standard ore-dressing methods does not appear promising. The use of such ores depends on the successful development of leaching or pyrometallurgical processes.

The manganiferous deposits of the Olympic Peninsula of Washington are largely manganese silicates. Ore-dressing methods in a few instances can be used to reject some of the gangue, but in general such methods fail. It is possible that some of the ores from the district may be used for the manufacture of silicomanganese or silicospiegel without concentration. Such methods have not, however, been developed.

The supplies of ferruginous manganese ores, manganiferous iron ores, and zinc residues from the plants of the New Jersey Zinc Co. are believe to be entirely adequate to fill the requirements for the production of spiegeleisen and manganiferous pig iron. The adequacy of the reserves of ore of this type have never been seriously questioned.

As in the past, Georgia, Virginia, and New Mexico will continue to produce manganese ore. The amount will depend on the demand.

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